TEXT BOOK OF

QUANTITATIVE INORGANIC ANALYSIS

KOLTHOFF I.M.

C-T MYSORE
28
extbook of quan

FLNS

39

TEXTBOOK OF QUANTITATIVE INORGANIC ANALYSIS

TEXTBOOK OF QUANTITATIVE INORGANIC ANALYSIS

BY

I. M. KOLTHOFF, PH. D.
PROFESSOR OF ANALYTICAL CHEMISTRY
UNIVERSITY OF MINNESOTA

AND

E. B. SANDELL, PH. D.
ASSISTANT PROFESSOR OF ANALYTICAL CHEMISTRY
UNIVERSITY OF MINNESOTA

CENTRAL FOOD TECHNOLOGICAL RESEAR
15 FEB 1951
LIBRARY
MYSORE.

REVISED EDITION

LONDON
MACMILLAN & CO. LTD
1950

1281

*This book is copyright in all countries
which are signatories to the Berne Convention*

First English Edition 1950

E1,1:3;R
N50

1281

CFTRI-MYSORE
1281
Textbook of quan.

PRINTED IN GREAT BRITAIN BY
MORRISON AND GIBB LIMITED, LONDON AND EDINBURG

Ex Pondere et Numero Veritas

PREFACE TO REVISED EDITION

In the new edition of this text the subject matter and its organization remain essentially the same as in the first edition. However, numerous changes and additions have been made to keep the book up to date. Fuller treatment has been given organic reagents, spectrophotometry, errors, and other topics; and a discussion of amperometric titrations has been introduced. The chapters on the formation and properties of precipitates, coprecipitation phenomena, and the theory of electroanalysis have been revised. Tables of atomic weights, gravimetric factors, and four-place logarithms have been placed on a folder, fitting in a pocket in the back of the book, to permit their use by students in examinations as well as to provide a handy form for use in the laboratory New problems have been added. In short, the text has undergone thorough revision, and the authors hope that the aims and objects of the first edition are retained in the second.

We sincerely appreciate the comments and criticisms generously offered by the teachers who used the first edition in their classes. Their suggestions have been carefully considered. Whenever a decided majority expressed a desire for certain changes, such changes were made in the text. There was a decided divergence of opinion among various teachers concerning a number of topics. Some thought that they could be omitted, others that they should be expanded. When such a discrepancy in views was apparent, we strove to reach a compromise.

We invite further suggestions for the improvement of the book.

I. M. Kolthoff
E. B. Sandell

Minneapolis, Minn.
June, 1943

PREFACE TO FIRST EDITION

A number of useful introductory texts in quantitative chemical analysis are available. No doubt every author of such a text is confronted with the perplexing problem of how much theory and how much practical work should be included. The compromise to which he is forced may or may not satisfy other teachers. An elementary textbook in quantitative analysis is necessarily limited in its scope, and many subjects of importance in this branch of chemistry cannot be treated. On the other hand, the advanced works in the field usually deal with highly specialized branches of the subject or selected topics, and there is little opportunity for the discussion of the broad fundamentals in a satisfactory way, at least not without repetition of much elementary matter which belongs in an introductory course. It seemed desirable to the authors to have available a book that could be used as an introductory text and which in addition would have the more or less comprehensive character of an advanced textbook, so that it would be suitable for use in beginning and advanced courses in analytical chemistry. With this aim in mind the authors have written the present work, in which there is contained material designed to make the student familiar with the fundamental theories of the subject, the practical methods of working, and the most important classical procedures. Highly specialized methods of analysis based on the measurement of physico-chemical properties (conductometric and potentiometric titrations, gas analysis, nephelometry, spectrography, etc.) could naturally not be treated at length, but enough is said concerning these to enable the student to appreciate the advantages of such methods, and a sufficient number of references is given to serve as a starting point for him who is interested.

In writing this text, it has been our aim to offer a balanced outline of the theoretical and practical aspects of inorganic quantitative analysis. There appears to be a tendency to exaggerate the significance of "theory" at the expense of practical work in chemical analysis. It must be realized that one of the most important ends of a course in quantitative analysis is the familiarization of the student with the procedures of analysis. The selection of practical exercises should be such that the student be acquainted with the important methods, be well trained in the quantitative technique, and be given an opportunity to develop confidence in his work. Mastery of practical analytical chemistry is of such fundamental importance in both pure and applied chemistry and other natural sciences that no student — however excellent may be his grasp of the theoretical principles involved — should be "passed" in an introductory course unless he can make analyses satisfactorily. The authors do not wish to convey the impression that the student should be educated merely as an analyst skilled in the art and ignorant in the science. A proper balance should be our goal. A course in quantitative analysis can be satisfactory from the chemical viewpoint only when the student is taught and trained to understand and interpret the phenomena he encounters in his practical work. Theory and practice should go hand in hand. Many chemical students are faced in later life with analytical problems of which the solution is not to be found in reference works but which can be solved by a rational and intelligent application of the principles of the subject.

Taking into account the difficulties that the beginning student must encounter on being introduced to a subject which is entirely new to him, it seems to the authors that from the didactic point of view gravimetric analysis should precede volumetric analysis. The theory of the former is much simpler than that of the latter. Therefore in beginning with gravimetric analysis, the instructor can gradually develop the theoretical fundamentals of quantitative analysis without overburdening the student at the start. In general it is inadvisable to have the student make determinations before the theory underlying them has been offered.

Considering the scope of the present text, a few words may be said concerning the material to be covered in a beginning and an advanced course. It must be stated at once that it is not possible to draw a hard and fast line between what may be called elementary and what may be called advanced material. The previous chemical training of the class and the ultimate use the student is expected to make of quantitative analysis are decisive factors in the selection of material for a beginning course. However, in order to facilitate the use of the present book for instructional purposes, the authors have made use of three different types of print, viz.:

(1) the finest to indicate material which is more or less informative in character (reagents, apparatus, technique of operations, etc.),

(2) an intermediate type to indicate material of advanced character, and

(3) the largest for material to be offered in an elementary course.

It must be emphasized that the size of the print does not designate the relative importance of the subject matter. Just because a section is set in fine type does not signify that it can be passed over. On the contrary, some very important material from the practical standpoint has been placed in fine print, as a casual examination will show. For example, the student should be expected to be familiar with the chapter on the technique of common operations before beginning any work in the laboratory. Expressed somewhat roughly, the beginning student should *read* the sections in fine print and should *study* those in ordinary print. Naturally the classification of the material in the manne described is more or less an arbitrary one. Various "theoretical" chapters have been put in "advanced" type. Although some of this material might well be covered in a beginning course, especially one for those students not planning to take an advanced course, it seems desirable not to overload the student in an introductory course with too much theoretical matter. Of fundamental importance is the mass-action law and its application to solutions of electrolytes, especially in volumetric analysis where an understanding of the procedures can be gained only by mastery of the theory of electrolytic solutions. An advanced course in analytical chemistry — which it seems to the authors should be made a requirement for all students in chemistry — is best offered after the student has completed a course in physical chemistry. Then the acquisition of the fundamental theory should become a relatively easy matter, and the student's interest in the multifold problems of analytical chemistry will be stimulated. Especially in a more advanced course the student will appreciate the possibilities of a rational application of physical and organic chemistry to the development of new methods and the improvement of procedures. Accordingly, the chapters on the properties of precipitates, adsorption and coprecipitation, water in solids, electroanalysis, physicochemical determination of the end point, colorimetry, physicochemical methods, etc. should preferably be reserved for a later stage when the student has made the acquaintance of physical chemistry.

Although it is impossible and undesirable to differentiate sharply between practical material to be covered in a beginning and an advanced course, the authors offer the following outline of laboratory work as a suggestive one for an elementary course:

Gravimetric analysis: Indirect determination of water in a hydrated salt; calibration of weights;[1] determination of chloride, of iron, of sulfate, of calcium, magnesium, and carbon dioxide in limestone, of phosphate, of silica in a mineral or rock, and of copper electrolytically.

Volumetric analysis: Calibration of volumetric glassware.

Acidimetry and alkalimetry: Preparation of standard hydrochloric acid and sodium hydroxide solutions (1 N, 0.1 N, 0.01 N), standardization of 0.1 N acid and 0.1 N base, Exercises (p. 555), titration of a weak acid, determination of sodium bicarbonate and sodium carbonate in a mixture or analysis of soda ash, determination of ammonia in an ammonium salt.

Precipitation analysis: Preparation and standardization of standard solutions for argentimetry (silver nitrate, sodium chloride, potassium thiocyanate); titration of chloride according to Mohr, Volhard, and with an adsorption indicator.

Oxidation-reduction methods: Preparation and standardization of potassium permanganate, determination of calcium; preparation of standard potassium dichromate, determination of iron in an iron ore with dichromate; preparation of standard potassium bromate, titration of arsenic trioxide.

Iodometry: Preparation of standard solutions, standardizations, Exercises (p. 626), determination of available chlorine in bleaching powder, determination of copper in an ore.

A fair number of problems, most of them with answers, have been included. It is to be expected, however, that the instructor will supplement these with many of his own and drill the student in quantitative calculations. It has not been thought necessary to go into the subject of calculations in any great detail in this volume. This highly important phase of the subject must be left to the instructor for elucidation and elaboration.

---

[1] Calibration of weights is best made after the student has acquired some familiarity with the balance. Preferably calibration should be reserved for an advanced course.

No training in analytical chemistry can be considered sati factory which does not give the student some opportunity familiarize himself with the journal literature and standard refe ence books. For this reason rather frequent literature citatio are given in this text. In advanced courses especially, the studen should be encouraged to refer frequently to the original sources.

It does not seem to be generally realized that analytical chem istry is one of the fundamental branches of the science. Th authors express the hope that books of the nature of the presen one will aid in the recognition of the importance of quantitativ analysis.

We will be grateful to everyone who will offer suggestions for th improvement of the book.

I. M. Kolthoff
E. B. Sandell

Minneapolis, Minn.
February, 1936

ACKNOWLEDGMENTS

In writing this book we have availed ourselves of pertinent material wherever it was to be found. In those cases in which we are specifically indebted to the work of others, we have endeavored to make proper acknowledgment by referring to the source of the information. The classic work *Applied Inorganic Analysis* of Hillebrand and Lundell was consulted freely in the writing of certain procedures of analysis. We have drawn heavily upon Lundell, Hoffman, and Bright's *Chemical Analysis of Iron and Steel* in the preparation of the chapter on steel analysis. Likewise we are under obligations to the following for most of the material in the chapter on rock analysis: Hillebrand, *The Analysis of Silicate and Carbonate Rocks;* Washington, *The Chemical Analysis of Rocks;* and the above-mentioned work of Hillebrand and Lundell.

For assistance rendered or suggestions offered, we wish to express our thanks to Doctors R. B. Ellestad, F. H. Hurley, William MacNevin, Lyle Overholser, V. A. Stenger, August Willman, and Henry Yutzy, and to Messrs. George Matsuyama and Leo Safranski. We are grateful to Dr. E. J. Meehan for his aid in the preparation of an outline of spectrophotometry and to Dr. J. J. Lingane for reading the manuscript of the first edition and testing certain points of procedure. To Dr. D. N. Hume we are greatly indebted for the critical reading of the galley proof of the revised edition. Finally we wish to express our appreciation to the late Prof. N. Schoorl of the University of Utrecht for valuable suggestions and to Dr. I. W. Geiger of the University of Minnesota for his interest in the work.

I. M. K.
E. B. S.

Chemical Analysis
Analytical Chemistry
[illegible]

TABLE OF CONTENTS

HAPTER PAGE
I. INTRODUCTION 1
II. STOICHIOMETRY. EXPRESSION OF RESULTS 12

GRAVIMETRIC ANALYSIS

III. GRAVIMETRIC ANALYSIS: INTRODUCTION 23

Theoretical Part

IV. THE MASS-ACTION LAW. (DISSOCIATION OF ELECTROLYTES. HYDROGEN-ION CONCENTRATION OF VARIOUS SOLUTIONS) 32
V. SOLUBILITY AND SOLUBILITY PRODUCT 48
VI. QUANTITATIVE SEPARATIONS 63
VII. THE FORMATION AND PROPERTIES OF PRECIPITATES . 93
VIII. COPRECIPITATION PHENOMENA 110
IX. WATER IN SOLIDS. (EFFLORESCENCE AND DELIQUESCENCE. PREPARATION OF HYDRATES WITH A DEFINITE AMOUNT OF WATER OF CRYSTALLIZATION. ADSORPTION OF WATER VAPOR. ESSENTIAL AND NONESSENTIAL WATER) 127
X. THEORY OF ELECTROANALYSIS 140

Practical Part: General

XI. REAGENTS 162
XII. APPARATUS 174
XIII. BALANCE, WEIGHTS, AND WEIGHING 195
XIV. TECHNIQUE OF COMMON OPERATIONS OF QUANTITATIVE ANALYSIS 235
XV. ERRORS IN QUANTITATIVE ANALYSIS 262

Gravimetric Determinations

XVI. DETERMINATION OF WATER 299
XVII. DETERMINATION OF CHLORINE IN SOLUBLE CHLORIDES 307
XVIII. DETERMINATION OF IRON 315
XIX. DETERMINATION OF ALUMINUM 324
XX. DETERMINATION OF SULFUR AS BARIUM SULFATE . . 329

CHAPTER
XXI. Determination of Calcium
XXII. Determination of Magnesium
XXIII. Analysis of Limestone
XXIV. Determination of Phosphorus
XXV. Determination of Silica
XXVI. Determination of Sodium and Potassium
XXVII. Electrolytic Determinations

VOLUMETRIC ANALYSIS

XXVIII. General Discussion of Volumetric Analysis

Theoretical Part

XXIX. Theory of Acidimetry and Alkalimetry
XXX. Theory of Precipitation and Complex-Formation Analysis
XXXI. Theory of Oxidation-Reduction Reactions
XXXII. Physico-chemical Determination of the End Point. Electrometric Titrations

Practical Part

XXXIII. Volumetric Apparatus and Its Use

Volumetric Determinations

XXXIV. Acidimetry and Alkalimetry
XXXV. Argentimetric and Mercurimetric Determinations
XXXVI. Reagents Used in Oxidation-Reduction Titrations
XXXVII. Permanganimetric Methods
XXXVIII. Titrations with Potassium Dichromate and Ceric Sulfate
XXXIX. Iodimetry and Iodometry
XL. Potassium Bromate and Calcium Hypochlorite as Standard Reagents

PHYSICO-CHEMICAL METHODS

XLI. Colorimetry and Spectrophotometry
XLII. Methods in Quantitative Inorganic Analysis

ANALYSES OF COMPLEX MATERIALS

XLIII. Analysis of Brass
XLIV. Analysis of Steel
XLV. Analysis of Silicate Rocks

APPENDIX

PAGE
Density of Water 764
Approximate Densities and Molarities of Concentrated Acids and Ammonia 764
Densities of Acids and Ammonia at 20° C. 765
Index of Authors 767
Index of Subjects 776

Atomic Weights, Four-Place Logarithms, and Gravimetric Factors . . . . . *Folder in Pocket at rear*

TEXTBOOK OF QUANTITATIVE INORGANIC ANALYSIS

CHAPTER I

INTRODUCTION

> *Analytical chemistry, or the art of recognizing different substances and determining their constituents, takes a prominent position among the applications of the science, since the questions which it enables us to answer arise wherever chemical processes are employed for scientific or technical purposes. Its supreme importance has caused it to be assiduously cultivated from a very early period in the history of chemistry, and its records comprise a large part of the quantitative work which is spread over the whole domain of the science.* — Wilhelm Ostwald (1894).

ualitative and quantitative analysis.

Analytical chemistry comprises qualitative and quantitative nalysis. The aim of qualitative analysis is the detection and dentification of the constituents of a compound or a mixture of ompounds or elements, whereas the determination of the percentage or molecular composition of a sample is the province of quantitative analysis.

Many of the reactions of qualitative analysis can be and are, by efinement and regulation of conditions, made the basis of quantitative processes. However, a procedure which has proved to be quite useful in qualitative analysis is not always applicable to quantitative analysis. In qualitative analysis it is often immaterial whether in a separation part of the constituent to be sought in the filtrate is retained in the precipitate. Therefore separations which have been found useful in qualitative analysis must be critically tested before application to quantitative analysis. In addition t may be said that the quantitative branch of the science makes use of reactions that find little or no application in the qualitative field. If the nature of the sample is entirely unknown, a qualitative examination must usually precede the quantitative analysis.

Not infrequently the composition of the sample is known from the origin of the latter, and then the quantitative analysis can often be made without a preliminary qualitative examination. A qualitative analysis is of the greatest aid in deciding the method to be followed in the quantitative analysis. Many quantitative procedures for a given element will yield erroneous results when certain other elements are present in the sample analyzed; and they must therefore be modified to eliminate, or at least reduce, the interference caused by other constituents. The determination of an element in a pure solution, i.e., a solution free from other substances, is a relatively simple matter; but the case is entirely different when the element in question is associated with others, as so often happens in practical analysis when complex natural materials and artificial products must be analyzed. In such cases, then, a qualitative analysis which reveals the constituents present and which indicates the relative amounts of these is often an indispensable preliminary to a proper quantitative analysis.

The importance of quantitative analysis and the scope of the subject.

A true understanding of any natural phenomenon is impossible without a knowledge of the quantitative relationships involved. Quantitative analysis has rendered most valuable services in the development of the science of chemistry and other sciences as well which make use of chemistry. The formulation of the fundamental laws of chemistry has been based largely on the results of quantitative analyses. For our knowledge of the composition of the earth and all it contains, and even of extraterrestrial matter, we are indebted to chemical analysis. Truly it has been said: "The sceptical chemist, and there is no other variety worthy of the name, draws conclusions regarding chemical materials under his scrutiny chiefly on the basis of quantitative chemical analysis, which in its proximate and ultimate forms, is the touchstone of all chemical hypothesis" (G. T. Morgan). In many branches of science, analytical chemistry plays an important rôle. It is, for example, indispensable to biology, mineralogy, petrography, and geochemistry, to mention but a few.

Quite apart from its fundamental position in the sciences, quantitative analysis occupies a most important place in human activities because of its utilitarian character. The value of raw materials such as ores, the suitability of a manufactured product for a given use, the control of a process of manufacture — these and many other problems require the application of quantitative chemical analysis for solution.

Since the extent of the subject is so great, a beginning course in quantitative analysis must necessarily be limited to a small portion of the field. It is convenient to divide quantitative chemical analysis into two great classes: inorganic and organic analysis, of which the first only is considered in an introduction to the subject. Indeed, inorganic analysis is itself of such vast extent that an introductory course can include only the fundamental theoretical principles of the subject, which are of the highest importance since they are universally significant, together with a few practical examples which illustrate the application of the principles and enable the student to acquire training in the quantitative technique.

The analytical chemist versus the chemical analyst.

The performance of a chemical analysis is an art requiring skill, care, and patience on the part of the analyst. After sufficient practice, any conscientious person can become a reliable analyst. This, however, does not mean that a good analyst is also a good analytical chemist. The former is one who has a good command of the quantitative technique, with or without a thorough understanding of the chemistry of the analytical processes involved.

An *analytical chemist* should be able to solve the problems of analysis, of any kind and complication, with which he may be confronted. He may be expected to develop his own methods of analysis when dealing with materials for which procedures are not described in the reference works or literature of chemical analysis. He should know the limitations of the methods applied and should be able to say why a given method of analysis may not give good results in certain cases. All this requires an understanding of the fundamental theory on which analytical chemistry is based, a knowledge of the analytical reactions of the elements, and an acquaintance with the various sources of error in the performance of an analytical determination. For this reason the theoretical fundamentals of the subject are considered with some thoroughness in this text. The theory of analytical chemistry does not constitute a special branch of chemistry; rather it comprises the application of our entire scientific knowledge to the particular purpose. An analytical chemist interested in the development of his field should keep abreast of the progress made in the other branches of the science, and even in other sciences.

Generally, a number of different methods of analysis are available for the determination of a particular constituent; usually they will yield results of different accuracy. In the performance of any analytical process, certain errors are always involved. By a practical application of our knowledge of the sources of error, we can reduce these errors to a minimum; and the result of the analysis will then closely approach the theoretical. Now, the analytical chemist should realize that the accuracy of the results desired should be governed largely by the purpose for which the analysis is made and should select his method and regulate the details of procedure accordingly. In the determination of atomic weights of elements, all possible precautions are taken in order to approach the true values as closely as possible; and no expenditure of time and labor is spared. On the other hand, a physiological chemist wishing to know, let us say, the chloride content of a sample of blood is usually satisfied if the results of the determination are within a few per cent of the truth. Quite intentionally an analytical chemist may, and indeed should, choose rapid, simple, but not necessarily highly accurate methods when results of great accuracy are not required or when time is an important factor. No general rules can be given regarding this matter because the accuracy desired or demanded varies from case to case.

In this text only the more exact methods of analysis are considered in most cases. This is done with the following objects in mind: to acquaint the student with the exact methods of analytical chemistry in order that he may gain self-confidence in the reliability of his work and also acquire practically useful knowledge, to impress upon him the various sources of error in chemical analysis, and to show the close relationship between an understanding of the theoretical fundamentals and the methods of reducing errors.

Anyone who has acquired sufficient skill to make an exact analysis satisfactorily can adapt himself to the performance of a less accurate one — but the reverse is not true.

The methods of quantitative analysis.

The determination of a substance in quantitative chemical analysis is based on the measurement of a physical or chemical property of the substance, the magnitude of which is a function of the amount present.

For purposes of classification four different groups of methods of analysis may be distinguished:

1. ***Gravimetric analysis.*** In this class of methods the constituent to be determined is isolated as such or, more often, as a compound which contains a definite known percentage of the constituent, which is then weighed. The separation leading to the isolation can be made by physical or chemical means, usually by the latter, since these afford more or less specific separations; and this is what is greatly desired, since the sample may be composed of many substances. The most important method of isolation of the desired constituent involves its *precipitation* by the addition of an excess of a reagent which forms with it a very slightly soluble compound. The precipitated substance is weighed as such; or it may be transformed into another substance of known composition, and this is then weighed. The methods of gravimetric analysis are considered in detail in Chapter III.

2. ***Volumetric*** (***titrimetric***) ***analysis.*** In volumetric analysis the constituent is allowed to react with a reagent which is added in the form of a solution of known concentration (standard solution). By methods to be described later, the point at which an equivalent amount of the reagent has been added is determined; and the amount of the constituent can then be calculated from the volume of standard solution added in the titration.[1] See Chapter XXVIII.

3. ***Physico-chemical analysis*** (see Chapter XLII). Here the constituents are determined by the measurement of a physico-chemical property such as density, refractive index, or color. In *colorimetry*, for example, the substance to be determined is transformed into a colored compound, and the color intensity of the solution is compared with a standard, using a colorimeter, or is measured with a spectrophotometer (p. 662). In *nephelometry*, the unknown is converted into a slightly soluble compound which is kept in suspension; the amount of the latter is found by comparing the intensity of the light scattered from the particles with that from a standard (p. 688). These methods are often suitable for very small amounts of substance.

---

[1] It should be noted that volumetric methods, in the sense that we use the term *volumetric* here, are distinguished from other methods by the fact that an equivalent amount of reagent is added in effecting the estimation. In the great majority of cases the amount of reagent required is found from the volume of the solution, whence the name. However, it is also possible to weigh the solution added, which as a matter of fact is done in very exact "volumetric" analysis. A better name for "volumetric" methods would be *titrimetric*, but the former term has firmly established itself in the language as a synonym for *titrimetric*.

4. *Gasometric analysis.* The amount of the substance being determined is found from the volume of a gas at a known temperature and pressure. The gas may be the substance itself or one formed from it.

Distinction may be made between *macro* and *micro* methods of analysis. The first involve weighing or measuring relatively large amounts of substance (weight of sample usually greater than 0.05 or 0.1 g.). In micro and semi-micro methods much smaller amounts of substance are worked with (samples of 1 to 50 mg. in the usual case). The latter methods are of relatively recent development in analytical chemistry and find special application when the amount of sample available is very small. As far as the theoretical principles are concerned, there is no difference between macro and micro quantitative analysis. The difference is merely one of the apparatus used and the technique followed. Gravimetric, volumetric, gasometric, and physico-chemical methods can all be adapted to microchemical work. Some physico-chemical methods, especially the colorimetric, nephelometric, spectrophotometric, and spectroscopic, are especially useful for the determination of micro quantities of constituents and can be so applied without special change in technique.

BIBLIOGRAPHY OF QUANTITATIVE ANALYSIS

The following list is not intended to be complete. It contains, however, most of the modern well-known works, especially those in the English language.

I. General Works on Quantitative Analysis
  A. Theory of Quantitative Analysis[2]
    H. Bassett, *The Theory of Quantitative Analysis*, Routledge, London, 1925.
    W. Ostwald, *The Scientific Foundations of Analytical Chemistry*, 3d English ed., translated by G. W. Gowan, Macmillan and Co., London, 1908.
    T. B. Smith, *Analytical Processes*, Arnold, London, 2d ed., 1940.

---

[1] Regarding the literature of chemistry in general, see E. J. Crane and A. M. Patterson, *The Literature of Chemistry*, John Wiley and Sons, New York, 1927; and M. G. Mellon, *Chemical Publications*, McGraw-Hill Book Co., New York, 2d ed., 1940; and B. A. Soule, *Library Guide for the Chemist*, McGraw-Hill Book Co., New York, 1938. These books contain sections on the literature of analytical chemistry.

[2] Various introductory texts of quantitative analysis contain more or less information on the theory of analytical chemistry. The list of these books is a long one, and it is therefore omitted here. See the lists of H. H. Willard and N. H. Furman, *Elementary Quantitative Analysis*, Van Nostrand Co., New York; and H. A. Fales and F. Kenny, *Inorganic Quantitative Analysis*, Appleton-Century Co., New York, 1939.

B. Gravimetric and Volumetric.[1] (The following are mostly reference works.)

- H. Biltz and W. Biltz, *Ausführung quantitativer Analysen*, S. Hirzel, Leipzig, 1930.
- A. Classen, *Handbuch der analytischen Chemie*, Vol. II (Quantitative), 9th ed., F. Enke, Stuttgart, 1924.
- G. Déniges, *Précis de chimie analytique*, A. Maloine et Fils, Paris, 1920.
- C. R. Fresenius, *Quantitative Analysis*, 2 vols., translated by A. L. Cohn, John Wiley and Sons, New York, 1908.
- *Gmelins Handbuch der anorganischen Chemie*, Verlag Chemie G.m.b.h., Berlin. Contains sections on analytical chemistry of the elements.
- F. A. Gooch, *Methods in Chemical Analysis*, John Wiley and Sons, New York, 1929.
- W. Herz (editor), *Sammlung chemisch-technischer Vorträge*, F. Enke, Stuttgart, 1896–1935. (Some pertain to analytical chemistry.)
- W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*, John Wiley and Sons, New York, 1929.
- G. E. F. Lundell and J. I. Hoffman, *Outlines of Methods of Chemical Analysis*, John Wiley and Sons, New York, 1938.
- B. M. Margosches (editor), *Die chemische Analyse*, 33 vols., F. Enke, Stuttgart, 1907–1935. A series of monographs dealing with chemical, technico-chemical, and physico-chemical analysis. Since 1931 edited by W. Böttger.
- J. W. Mellor and H. V. Thompson, *A Treatise on Quantitative Inorganic Analysis*, C. Griffin and Co., London, 1938.
- A. D. Mitchell and A. M. Ward, *Modern Methods in Quantitative Chemical Analysis*, Longmans, Green and Co., London, 1932.
- A. Rüdisüle, *Nachweis, Bestimmung und Trennung der chemischen Elemente*, 7 vols., M. Drechsel, Bern, 1913–1929.
- W. W. Scott, *Standard Methods of Chemical Analysis*, 2 vols., 5th ed., D. Van Nostrand Co., New York, 1939. Vol. I deals with general quantitative analysis.
- E. P. Treadwell and W. T. Hall, *Analytical Chemistry*, Vol. II (Quantitative), 9th ed., John Wiley and Sons, New York, 1942.
- W. D. Treadwell, *Tabellen und Vorschriften zur quantitativen Analyse*, F. Deuticke, Leipzig, 1938.
- W. van Tongeren, *Gravimetric Analysis*, D. B. Centen, Amsterdam, 1937.

C. Volumetric

1. General

- H. Beckurts, *Die Methoden der Massanalyse*, Vol. I, 2d ed., F. Vieweg, Braunschweig, 1931.

---

[1] Of the works listed here, the treatise of Hillebrand and Lundell stands out as an authoritative work on the subject of chemical analysis; it embraces the analytical chemistry of practically all the elements and contains critically tested procedures of determination and separation. The Margosches series is valuable for its treatment of special subjects. The work of Rüdisüle is a comprehensive, but uncritical, compilation of analytical methods. Fresenius was once a standard work but is now out of date. The other books listed will be found more or less useful and have their place.

E. Brennecke, N. H. Furman, H. Stamm, R. Lang, and K. Fajans, *Newer Methods of Volumetric Analysis*, translated by R. E. Oesper, D. Van Nostrand Co., New York, 1938.

A. Classen, *Theorie und Praxis der Massanalyse*, Akademische Verlagsgesellschaft, Leipzig, 1912.

G. Jander and K. F. Jahr, *Massanalyse*, 2 vols., W. de Gruyter and Co., Berlin and Leipzig, 1935.

I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis*, Vol. I *Theoretical Fundamentals*, 2d ed., 1942, Vol. II *Practice of Volumetric Analysis*, 2d ed., 1943, Interscience Publishers, New York.

F. Sutton, *Volumetric Analysis*, 12th ed., P. Blakiston's Son and Co., Philadelphia, 1935.

2. Special

G. S. Jamieson, *Volumetric Iodate Methods*, Chemical Catalog Co., New York, 1926.

E. Knecht and E. Hibbert, *New Reduction Methods in Volumetric Analysis*, Longmans, Green and Co., London, 1918.

N. Bjerrum, *Die Theorie der alkalimetrischen und azidimetrischen Titrierungen*, F. Enke, Stuttgart, 1914. (One of the Sammlung chemischer und chemisch-technischer Vorträge.)

II. Works on Specialized Methods of Analysis

A. Electroanalysis

A. Classen and H. Cloeren, *Quantitative Analysis by Electrolysis*, translated by W. T. Hall, 5th ed., John Wiley and Sons, New York, 1919.

A. Classen and H. Danneel, *Quantitative Analyse durch Electrolyse*, 7th ed., J. Springer, Berlin, 1927.

A. Fischer, *Electroanalytische Schnellmethoden*, 2d ed. by A. Schleicher, F. Enke, Stuttgart, 1926.

H. J. S. Sand, *Electrochemistry and Electrochemical Analysis*. Vol. II *Gravimetric Electrolytic Analysis and Electrolytic Marsh Tests*, Blackie and Son, London and Glasgow, 1940.

E. F. Smith, *Electroanalysis*, 4th ed., P. Blakiston's Son and Co., Philadelphia, 1907.

B. Electrometric Methods. (See Chapter XXXII, p. 503.)

C. Gasometric Analysis. (See Chapter XLII, p. 680.)

D. Microanalysis

A. A. Benedetti-Pichler, *Introduction to the Microtechnique of Inorganic Analysis*, John Wiley and Sons, New York, 1942.

E. M. Chamot and C. W. Mason, *Handbook of Chemical Microscopy*, 2d ed., 2 vols., John Wiley and Sons, New York, 1938 and 1940. (Chapter 14 of Vol. I is devoted to quantitative microscopical analysis.)

F. Emich, *Lehrbuch der Mikrochemie*, 2d ed., J. F. Bergmann, München, 1926.

F. Emich, *Michrochemical Laboratory Manual*, translated by F. Schneider, John Wiley and Sons, New York, 1932.

A. Friedrich, *Die Praxis der quantitativen organischen Mikroanalyse*, F. Deuticke, Leipzig and Vienna, 1933.

J. B. Niederl and V. Niederl, *Micro-methods of Quantitative Organic Elementary Analysis*, 2d ed., John Wiley and Sons, New York, 1942.

F. Pregl, *Quantitative Organic Microanalysis*, translated by E. Fyleman, 2d English ed., P. Blakiston's Son and Co., Philadelphia, 1930.

C. Weygand, *Quantitative analytische Mikromethoden der organischen Chemie in vergleichender Darstellungen*, Akad. Verlagsgesellschaft, Leipzig, 1931.

E. Physico-chemical Methods. (See Chapter XLII.)

III. Works on Analysis of Special Materials. (Highly specialized works are not included.)

A. General Technical Analysis

A. H. Allen, *Commercial Organic Analysis*, 8 vols., 5th ed., P. Blakiston's Son and Co., Philadelphia, 1923–1930.

Book of Standards, American Society for Testing Materials, Philadelphia, 1933.

E. Berl and G. Lunge, *Chemisch-technische Untersuchungsmethoden*, 5 vols., 6th ed., J. Springer, Berlin, 1931–1934.

R. C. Griffin, *Technical Methods of Analysis*, McGraw-Hill Book Co., New York, 1927.

G. Lunge and C. A. Keane, *Technical Methods of Chemical Analysis*, 3 vols., 2d ed. edited by C. A. Keane and P. C. L. Thorne, D. Van Nostrand Co., New York, 1924–1931.

W. W. Scott, *Standard Methods of Chemical Analysis*, 2 vols., 5th ed., D. Van Nostrand Co., New York, 1939. Vol. II deals with the analysis of commercially important materials.

V. Villavecchia, *Treatise on Applied Analytical Chemistry*, translated by T. H. Pope, J. and A. Churchill, London, 1918.

B. Agricultural Materials, Foods, etc.

A. Bömer, A. Juckenack, and J. Tillmans, *Handbuch der Lebensmittelchemie*, 9 vols., Hirschwaldsche Buchhandlung, Berlin, 1933–

C. A. Browne and F. W. Zerban, *Physical and Chemical Methods of Sugar Analysis*, 3d ed., John Wiley and Sons, New York, 1941.

H. E. Cox, *Chemical Analysis of Foods*, 2d ed., J. and A. Churchill, London, 1938.

M. B. Jacobs, *Chemical Analysis of Foods and Food Products*, D. Van Nostrand Co., New York, 1938.

A. E. Leach and A. L. Winton, *Food Inspection and Analysis*, John Wiley and Sons, New York, 1924.

J. Lewkowitsch, *Chemical Technology and Analysis of Oils, Fats, and Waxes*, 3 vols., 6th ed., Macmillan and Co., London, 1921–1923.

E. G. Mahin and R. H. Carr, *Quantitative Agricultural Analysis*, McGraw-Hill Book Co., New York, 1923.

W. W. Skinner *et al.*, *Official and Tentative Methods of Analysis*, Association of Official Agricultural Chemists, 5th ed., Washington, 1940.

V. Villavecchia, *Treatise on Applied Analytical Chemistry*, 2 vols., translated by T. H. Pope, J. and A. Churchill, London, 1918. (Vol. II treats chiefly of food analysis.)

H. W. Wiley, *Principles and Practice of Agricultural Analysis*, Chemical Publishing Co., New York, 1926.

A. G. Woodman, *Food Analysis*, 4th ed., McGraw-Hill Book Co., New York, 1941.

C. H. Wright, *Agricultural Analysis*, T. Murby and Co., London, 1938.

(See also the works under III A.)

C. Alloys

1. Ferrous. (See p. 730.)
2. Non-ferrous. (See p. 704.)

D. Minerals and Ores

F. G. Hills, *The Technical Analysis of Ores and Metallurgical Products*, Chemical Publishing Co., New York, 1937.

R. B. Moore *et al.*, *Analytical Methods for Certain Metals Including Cerium, Thorium, Molybdenum, Tungsten, Radium, Uranium, Vanadium, Titanium, and Zirconium*, Bureau of Mines, Bulletin 212, Government Printing Office, Washington, 1923.

W. R. Schoeller, *The Analytical Chemistry of Tantalum and Niobium*, Chapman and Hall, London, 1937.

W. R. Schoeller and A. R. Powell, *The Analysis of the Minerals and Ores of the Rarer Elements*, C. Griffin and Co., London, 1940.

W. M. Thornton, *Titanium*, Chemical Catalog Co., New York, 1927.

A. J. Weinig and W. P. Schoder, *Technical Methods of Ore Analysis for Chemists and Colleges*, John Wiley and Sons, New York, 1939.

For Rock Analysis, see p. 733.

E. Reagents. (See p. 163.)

F. Water. (Only a few works are included.)

Standard Methods for the Examination of Water and Sewage, American Public Health Association, New York.

Ohlmüller and Spitta, *Untersuchung und Beurteilung des Wassers und Abwassers*, 5th ed., J. Springer, Berlin, 1931.

IV. Journals. The following journals are devoted to general or specialized analytical chemistry:

The Analyst.

Annales de chimie analytique et de chimie appliquée et revue de chimie analytique réunies.

Annales des falsifications et des fraudes.

Industrial and Engineering Chemistry, Analytical Edition.

Journal of the Association of Official Agricultural Chemists.

Mikrochemie ver. Mikrochimica Acta.

Zeitschrift für analytische Chemie.

Zeitschrift für Untersuchung der Lebensmittel.

In addition, many papers on chemical analysis appear in the general chemical journals (or science journals), which are too numerous to list here. (See E. J. Crane and A. M. Patterson, *Literature of Chemistry*, and also M. G. Mellon, *Chemical Publications*.) Reference may also be made to the reports of the International Congress of Applied Chemistry.

Special attention is called to the abstracting journals, which are of extreme value in literature searches. As general abstracting journals, *Chemical Abstracts* (published by the American Chemical Society) and the *Chemisches Zentralblatt* (published by the Deutsche Chemische Gesellschaft) deserve mention. Some of the analytical journals mentioned above contain abstracts of the analytical literature.

Yearbooks, such as the *Annual Reports on the Progress of Chemistry* issued by the Chemical Society (London), and the *Annual Survey of American Chemistry*, may be referred to for recent progress in the analytical field.

V. Miscellaneous Publications

Public documents, especially of the U. S. Government, constitute a source of information on methods of analysis. A list of some of the bulletins dealing with analysis issued by the Federal bureaus may be found in the appendix of Griffin, *Technical Methods of Analysis* (see III A above). A list of the government publications can be obtained by addressing the Superintendent of Documents, Government Printing Office, Washington, D. C.

Certain institutions and industrial concerns publish their methods of analysis.

CHAPTER II

STOICHIOMETRY. EXPRESSION OF RESULTS

There are a few fundamental laws concerning the weight relationships of the elements in their compounds which are the basis of the methods of quantitative chemical analysis. These laws appear so self-evident to us that we often are hardly aware that the science of analysis is founded upon them.

Combining weights.

At the beginning of the nineteenth century Dalton pointed out that it is possible to assign to every element a relative weight with which that element enters into chemical combination. This weight is known as the combining weight of the element. Dalton's *Law of Combining Proportions* may be formulated as follows: *Elements combine in the ratio of their combining weights or of simple multiples of these weights.* This law includes the *Law of Definite Proportions* (Richter and Proust): *A definite chemical compound always contains the same elements united in the same proportion by weight.*

Assuming that the combining weight of hydrogen is unity, the combining weights of the other elements can be expressed on this basis. It should be realized that the combining weight of an element does not represent a constant. Thus, 1 g. of hydrogen combines with approximately 8 g. of oxygen to form H_2O and with approximately 16 g. to give H_2O_2. Comparing hydrogen chloride, water, and hydrogen sulfide, it is found that 1 g. of hydrogen combines with 35.5 g. of chlorine, 8 g. of oxygen, and 16 g. of sulfur respectively. It may be said then that 35.5 parts of chlorine, 8 parts of oxygen, and 16 of sulfur are equivalent. A chemical equivalent may be defined as the weight of an element which combines with or displaces a unit weight of hydrogen (cf. p. 434). It follows from the above that the equivalent weight of an element is not constant but depends upon the particular valence state of the element in the compound concerned. Thus we have seen that the chemical equivalents of oxygen are 8 and 16 respectively.

Since the introduction of the atomic theory of Dalton, it has been generally assumed that chemical compounds result from the union of atoms of elements, each of which has a definite weight.

Atomic weights.

The atomic weights of the elements may be defined broadly as the relative weights of the atoms of each. For certain reasons the atomic weight of oxygen is taken as 16.0000, and the atomic weights of the other elements are based on, or referred to, this value.

The atomic weight expressed in grams is called the gram-atom or gram-atomic weight. A gram-atom of oxygen is, accordingly, 16.0000 g. The molecular weight of a substance is equal to the sum of the atomic weights of its constituent elements, each atomic weight being multiplied by the number of atoms of each particular element present in the molecule. The molecular weight expressed in grams is called a gram-molecular weight or *mole*.[1]

The atomic weights then represent ratios of the weights of gram-atoms of the various elements compared to that of oxygen taken as 16.0000 g. Naturally an exact knowledge of atomic weights is of fundamental importance in analytical chemistry since they form the basis of all calculations involved in an analysis. The late Professor Theodore William Richards (1868–1928), professor at Harvard University, who received international recognition by being awarded the Nobel prize for his contributions, once expressed himself as follows in speaking of his work: "This field was chosen, not merely because I felt more competent in that direction than in any other, but also because atomic weights seemed to be one of the primal mysteries of the universe. They are values which no man by taking thought can change. They seem to be independent of place and time." (This was said before the discovery of radioactivity and isotopes.) "They are silent witnesses of the very beginning of the universe and the half-hidden, half-disclosed symmetry of the periodic system of the elements only enhances one's curiosity about them. Moreover, among the many properties possessed by an element, the atomic weight seems one of the most definite and precise. Hence in trying to satisfy a desire which had as its object the discovery of more knowledge concerning the fundamental nature of things, one naturally assigns to the atomic weight an important place."

The atomic weight of an element is found experimentally by determining its combining weight by the most accurate methods available. However, no analytical method is perfect, and therefore the values of the atomic weights are subject to slight errors. With the further development of improved experimental technique and of science, they may undergo slight changes with time. It is for this reason that each year the "Committee on Atomic Weights of the International Union of Chemistry," headed by Professor G. P. Baxter, Richards' successor at Harvard, gives a critical review of the progress made in atomic-weight work and fixes an internationally accepted table of atomic weights for each year. The last report and table are published in the J. Am. Chem. Soc. *63*, 850 (1941) by the members of the committee: G. P. Baxter (chairman), M. Guichard, O. Hönigschmid, and R. Whytlaw-Gray.

---

[1] The number of molecules in a mole of substance is constant and is given by Avogadro's number: 6.02×10^{23}.

From the analytical viewpoint it would perhaps be satisfactory to publish a table for the common elements every ten years, since the changes in the atomic weights of these during the last decade have been too small to affect the accuracy of an analytical result. The case is different for the rare elements, whose compounds are harder to obtain in a pure state. For example, the atomic weight of cesium given in 1933 was 132.81, in 1934, 132.91; of osmium, 190.8 in 1933 and 191.5 in 1934. The atomic weight of potassium changed from 39.10 (1933) to 39.096 (1934) or 0.01 per cent, a change negligibly small from the analytical standpoint.

With the discovery of the existence of isotopes of many common elements, the fundamental significance of ordinary atomic weights became questionable. The phenomenon of isotopy permits the occurrence of a number of chemically inseparable forms of an element, each possessing the same atomic number but differing in atomic mass. Since the common elements are composed of a number of isotopes in virtually constant proportions, it is clear that the ordinary atomic weight is not characteristic of a single atomic species but represents the average gram-atomic weight of a mixture of isotopes. Fortunately the isotopic composition of the common elements as found in nature is constant, except in rare instances; consequently the atomic weights also are found to be constant.

Originally it was thought that oxygen itself possessed no isotopes, and its atomic weight was taken as 16.0000. Recently it has been shown that ordinary oxygen contains extremely small amounts of the isotopes O^{17} and O^{18}. From the relative abundance of these isotopes, and taking the atomic weight of ordinary oxygen as 16.0000, the atomic weight of pure O^{16} has been calculated to be 15.9965 ± 0.0002. If one wished to relate all atomic weights to that of pure O^{16} it would be necessary to increase all ordinary atomic weights by 0.022 per cent. This practice is objectionable from the chemical point of view. For this reason the Committee on Atomic Weights of the International Union of Chemistry has decided to retain the atomic weight of "ordinary oxygen" as 16.0000 regardless of its isotopic composition. However, it should be understood that this adoption does not affect the fundamental value of the ordinary atomic weights in the least, since for chemical purposes we require the ratios of the weights of the gram-atoms of the elements as they occur in nature and not of the individual isotopes of which they are composed.

It is of interest to mention that water as it occurs in nature contains approximately one part of heavy water ($H^2_2O^{16}$) in 5000 parts of light water ($H^1_2O^{16}$), this ratio being virtually constant.

Stoichiometry.

A chemical equation is a symbolic statement of the quantitative relation between the reactants and the reaction products. Thus the chemical equation:

$$AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$$

indicates that 1 mole of silver nitrate reacts with 1 mole of sodium chloride to form 1 mole of silver chloride and 1 mole of sodium nitrate. If on mixing a solution of silver nitrate with a solution of sodium chloride the above reaction proceeds quantitatively to the right, the equation also indicates that 169.89 g. of silver nitrate react with 58.46 g. of sodium chloride to give 143.34 g. of (insoluble) silver chloride and 85.01 g. of sodium nitrate. Moreover, it indicates that 107.880 g. of silver ion react with 35.46 g. of chloride ion to yield 143.34 g. of silver chloride. Thus, it is an easy matter to calculate how many grams of silver chloride are formed from a g. of silver or a' g. of silver nitrate, or b g. of chloride or b' g. of sodium chloride. It may be stated also that the 143.34 g. of silver chloride formed are equivalent to 107.88 g. of silver and 35.46 g. of chloride respectively, or more generally w g. of silver chloride formed correspond to

$$\frac{107.88}{143.34}\,w \text{ g. of silver, and}$$

$$\frac{35.46}{143.34}\,w \text{ g. of chloride.}$$

If gases react or are reaction products, it is also possible to derive weight-volume relationships from equations. Avogadro's law (1811) states: *Under the same conditions of temperature and pressure, equal volumes of all gases contain the same number of molecules.* One mole of an ideal gas occupies 22.41 liters under standard conditions of temperature and pressure (0° C., pressure = 760 mm. of mercury).

The chemical reaction between calcium carbonate and hydrochloric acid takes place quantitatively under the proper conditions according to the equation:

$$CaCO_3 + 2\,HCl \rightarrow CaCl_2 + CO_2 + H_2O.$$

This means then that 1 mole or 100.08 g. of calcium carbonate yields 44.00 g. of carbon dioxide, the latter occupying a volume of 22.41 liters at 0° C. under the pressure of a normal atmosphere.

The volume V occupied by the dry gas at a temperature $t°$ C. and a pressure p is found from the gas law:

$$\frac{pV}{T} = \text{constant} = R$$

in which $T = (273 + t°)$.[1]

Expression of analytical results.

Chemical expression of results. The amount of a certain constituent in a given sample is calculated from the analytical results by methods that will be considered later. The question which concerns us at this point is: In what form shall the results of an analysis be reported? For example, calcium has been determined in a limestone. Shall it be reported as the element, the carbonate, or the oxide?

In general it may be said that wherever possible the element determined should be reported in the form in which it is present in the sample analyzed, unless there is a good reason for the contrary. Thus in reporting the result of a determination of nitrogen, it should be stated in the form of nitrate (NO_3^- or N_2O_5), nitrite (NO_2^- or N_2O_3), or ammonia (NH_3), depending upon the state or states in which the elements is present. The analysis of a simple salt may be reported in the ionic form (e.g., K_2SO_4 as K^+ and $SO_4^=$). If the composition of the sample is unknown and cannot readily be determined, the results are usually given in the form of the elements or their oxides. Often the purpose of the analysis decides the form in which the constituents are reported. Thus, the calcium content of a limestone is conveniently given in terms of calcium oxide if the material is to be used for the manufacture of lime, the iron content of an ore is preferably stated in terms of metallic iron, etc.

In the complete analysis of a complex sample containing oxygen it is generally preferable to report the elements in the form of their oxides (K as K_2O, Ca as CaO, Fe^{II} as FeO, Fe^{III} as Fe_2O_3, S as SO_3, P as P_2O_5, etc.). There are a number of reasons for this. Oxygen is never determined directly and must therefore be apportioned among the other constituents with which it exists in combination. The state of oxidation of the metals is readily shown in the statement of results. The sum of the acid and basic oxides (including water), expressed in per cent, must equal 100 in a perfect analysis. There is no objection to this mode of expression as long as all acid-forming elements of the sample may be considered to be present as acid oxides, but difficulties arise when the acid elements have no corresponding oxides (halides, sulfides, etc.). However, in such cases it is possible to report the non-conforming acid elements in the elemental form (Cl, S^{II}, etc.) and then deduct the oxygen equivalent of these elements from the summation (see p. 760) to obtain 100 per cent.

---

[1] Regarding the calculations of quantitative analysis see, for example, the following:

L. F. Hamilton and S. G. Simpson, *Calculations of Quantitative Chemical Analysis*, 3d ed., McGraw-Hill Book Co., New York, 1939. E. H. Miller, *The Calculations of Analytical Chemistry*, The Macmillan Co., New York, 1921. J. A. Wilkinson, *Calculations in Quantitative Chemical Analysis*, 2d ed., McGraw-Hill Book Co., New York, 1938. C. J. Engelder, *Calculations of Quantitative Chemical Analysis*, John Wiley and Sons, New York, 1939. S. B. Arenson, *How to Solve Problems in Quantitative Analysis*, T. Y. Crowell Co., New York, 1942.

The results of the analysis of a solution of electrolytes are generally expressed in terms of the ions present.

Numerical expression of results. It is the relative amount of a constituent in a sample that is of importance. Accordingly, in expressing the quantity of a constituent present in the sample analyzed, the following general expression is used:

$$\frac{q}{Q} \times c$$

where q = the quantity of constituent present in the sample,
Q = the quantity of the sample,
c = some factor.

The factor c is introduced in order that the result may be expressed in units of convenient magnitude.

If q and Q are both given in the same units of weight and c is put equal to 100, the result is the *percentage by weight* of constituent in the sample; if c is set equal to 1,000,000 and q and Q are expressed in the same weight units, the answer is the parts per million by weight of the constituent in the sample, and so on. The quantities q and Q may also be expressed in volume units, as we shall see.

Solids. When the sample analyzed is a solid, it is most usual to express the amount of the constituent in question in terms of percentage by weight:

$$\left(\frac{\text{weight of constituent}}{\text{weight of sample}} \times 100\right).$$

Sometimes when the relative amount of the constituent is very small, the result is stated in parts per million (p.p.m.) by weight. For example, if a 1 g. sample of potassium chloride is found to contain 0.002 mg. of lead, it is more convenient to express the lead content of the potassium chloride as 2 p.p.m. than as 0.0002 per cent.

Liquids. With liquid samples various modes of expression are possible:

(1) *Percentage by weight.* The number of parts of constituent in 100 parts of sample, both in the same weight units, is the weight percentage of the constituent in the sample. This expression may be designated by P_w^w.

(2) *Percentage by volume.* The number of parts by volume of a constituent in 100 volumes of sample at a specified temperature gives the volume percentage of that constituent (P_v^v). This mode of expression is often used when the constituent is a liquid or gas.

(3a) *Parts by weight* of constituent in 100 parts by volume of sample.

(3b) *Parts by volume* of constituent in 100 parts by weight of sample.

These may respectively be designated by P_v^w and P_w^v. The temperature must be specified in each case. The former expression may be used to designate the concentration of a solid or liquid in a liquid and the latter the volume of liquid (or gas) in a given weight of another liquid.

In general the expression P_w^w is preferable to the others because it is independent of the temperature. Evidently the following relations exist among these modes of expression if w is expressed in grams, v in milliliters, and density, d, in g. per ml.:

$$P_v^w = d_l P_w^w (d_l = \text{density of liquid sample}).$$

$$P_w^v = \frac{P_w^w}{d_c} (d_c = \text{density of liquid constituent}), \text{ and } P_v^v = \frac{d_s}{d_c} \times P_w^w.$$

There are other ways of designating the concentration of solutions which need not be considered here (cf. p. 32).

When the amount of constituent present in a solution is small, it is advantageous to express it in p.p.m. by weight or volume. Thus in the analysis of natural waters the ions are reported in p.p.m. For example, a water found to contain 0.030 g. of magnesium in one liter is said to have 30 p.p.m. of Mg^{++}, i.e., 30 parts by weight of Mg^{++} in 1,000,000 parts by volume of solution. Generally it makes but little difference in the case of a *dilute* solution whether the quantity of the latter is expressed in weight or volume, i.e., 997 g. of water at room temperature occupy a volume of *ca.* 1000 ml.

Gases. The composition of a gaseous mixture is commonly expressed in percentage by volume (P^v_v).

PROBLEMS

Note: In working these and following problems, the student should obtain the answers through his own train of reasoning and should avoid the mechanical use of formulas and equations.

1. One hundred milliliters of dry ammonia, measured at 25° and a pressure of 750 mm. of mercury, are absorbed in excess sulfuric acid. What weight of NH_4HSO_4 is produced? *Ans.* 0.4645 g.

2. Two liters of dry air (0°, 760 mm.) are passed over sodium hydroxide to absorb the carbon dioxide present. If a gain in weight of 1.2 mg. is observed, what is the percentage by volume of carbon dioxide in the air? *Ans.* 0.03 per cent.

3. Water at room temperature in equilibrium with the atmosphere is $1.5 \times 10^{-5}\ M$ in carbon dioxide. What are the weight and the volume (0°, 760 mm.) of carbon dioxide in a liter of such water? *Ans.* 0.66 mg., 0.34 ml.

4. Concentrated phosphoric acid containing 85 per cent of H_3PO_4 has a density of 1.69. Calculate the number of grams and moles of H_3PO_4 in one liter of acid. What is the molarity of the acid? *Ans.* 1437 g., 14.7 moles, 14.7 M.

5. What volume of concentrated hydrochloric acid having a density of 1.200 and containing 39.11 per cent of HCl is required to prepare (a) 1 liter of acid containing 20.01 per cent HCl (density 1.100), (b) 1 liter of 6 N acid? *Ans.* (a) 469.0 ml., (b) 466.2 ml.

6. If the density of anhydrous ethyl alcohol is 0.7939, what is the per cent by weight of alcohol in a 95 per cent by volume alcohol solution of density 0.8160? *Ans.* 92.43 per cent.

7. In a colorimetric determination of boron a sulfuric acid solution containing 98.5 per cent H_2SO_4 is required. It is to be prepared by adding fuming sulfuric acid containing 20 per cent free SO_3 to ordinary concentrated sulfuric acid containing 95 per cent H_2SO_4. How many grams of each are required to make 100 g. of the desired mixture of 98.5 per cent H_2SO_4?

8. Calculate the percentage composition of $CuSO_4 \cdot 5\ H_2O$ (Cu, SO_4, H_2O). *Ans.* Cu = 25.46, SO_4 = 38.47, H_2O = 36.07 per cent.

9. It is desired to prepare a sample containing 50.0 per cent Cl by mixing NaCl and KCl. In what ratio must the salts be mixed?

10. In the determination of ethyl alcohol in a liquid, a 25.00 ml. sample was taken at 20° (specific gravity of liquid = 1.030, 20°/4°), diluted to 150 ml., and the mixture distilled. One hundred milliters of distillate (containing all the alcohol in the original sample) was collected and its specific gravity determined; it was found to be 0.97953 (20°/4°), corresponding to 14.50 per cent alcohol by volume at 20° and 11.68 per cent by weight. Calculate:

(a) The percentage by weight of alcohol in the original sample.
(b) The percentage by volume at 20°.
(c) The number of grams of alcohol in 100 ml. of sample at 20°.

11. A hydrated cadmium salt contains 43.82 per cent Cd, 37.45 per cent SO_4 and 18.73 per cent H_2O. What is its formula?

12. What is the formula of a mineral containing 64.5 per cent SiO_2, 27.4 per cent Al_2O_3, and 8.4 per cent Li_2O? *Ans.* $LiAl(SiO_3)_2$ or $Li_2O \cdot Al_2O_3 \cdot 4\ SiO_2$.

13. What is the formula of a salt containing 54.4 per cent F, 12.8 per cent Al, and 32.8 per cent Na?

14. Berzelius in 1843 determined the atomic weight of calcium by converting pure calcium oxide into calcium sulfate by treatment with sulfuric acid, the excess of the latter being removed by strong heating. In a typical experiment 2.5040 g. of CaO yielded 6.0750 g. of $CaSO_4$. Assuming S = 32.06 and O = 16.00, calculate the atomic weight of Ca, neglecting air buoyancy.

Ans. 40.14.

15. Hönigschmid and Sachtleben (1929) determined the atomic weight of silver and barium by converting anhydrous barium perchlorate into barium chloride by heating and then finding the weight of silver required to precipitate the chloride in the latter. In one analysis 11.69950 g. $Ba(ClO_4)_2$ gave 7.24609 g. $BaCl_2$, which was found equivalent to 7.50692 g. Ag (all weights are vacuo weights). Calculate the atomic weight of silver and barium from these data, taking O = 16.0000 and Cl = 35.457. *Ans.* Ag = 107.882.

GRAVIMETRIC ANALYSIS

CHAPTER III

GRAVIMETRIC ANALYSIS: INTRODUCTION

Classification of methods used in gravimetric analysis.

In any direct gravimetric analysis, the constituent being determined is separated from the other constituents of the sample in the form of a pure phase which may be the constituent itself or a compound of known and definite composition; from the *weight* of the latter, the weight of the constituent sought is found. The separation, which must always precede the weighing of the constituent or a compound containing it, may be effected in a number of ways. The classification of gravimetric methods is based fundamentally on the methods of separation employed. In the following classification, which is a rough but convenient one practically, the methods are arranged in the order of their importance.

1. ***Precipitation methods.*** In a precipitation process the constituent being determined is precipitated as a very slightly soluble compound (or sometimes element), and the weight of the latter (or of the substance into which it may be advantageous to convert the precipitation form before weighing) is found.

For example, in determining chloride, a solution of the sample is treated with an excess of silver nitrate to precipitate silver chloride; the precipitate is filtered off, washed free of soluble substances, dried, and weighed as silver chloride. From the weight of the dried precipitate, the weight and percentage of chlorine as chloride are easily found (see below). Not infrequently the constituent in question is weighed in a form other than that in which it was precipitated. Thus, calcium is precipitated as calcium oxalate monohydrate but is preferably weighed as calcium oxide or calcium carbonate for reasons that need not be considered at this point. Electrolytic determinations, in which metals are separated as such on a cathode or in which some anions are deposited as slightly soluble salts on a particular metal anode (halides as silver halides on a silver anode), belong in the class of precipitation processes.

Precipitation methods are of the greatest importance because often they are more or less specific for the constituent being determined and are of general applicability.

2. *Volatilization or evolution methods.* Here one or more of the constituents of the sample is volatile or can be transformed into a volatile compound.

(1) *Direct methods.* In this subclass, the volatilized or evolved constituent is absorbed in a suitable medium, and the gain in weight of the latter is determined. The method is specific if no other volatile compounds which are absorbed by the medium are present. For example, water in a solid can be determined by heating the sample to the proper temperature and absorbing the volatilized water in a suitable desiccant such as anhydrous magnesium perchlorate. Even if a carbonate were present in the sample, the carbon dioxide evolved on heating would not interfere, since this gas is not retained by magnesium perchlorate (but would be by such basic desiccants as calcium oxide, which naturally could not be used in this case). Analogously, carbon dioxide present as carbonate or bicarbonate can be determined by treating the sample with an excess of acid and absorbing the gas in a suitable substance, such as soda-lime, after the gas stream has been led through a desiccant to remove water vapor. Hence we are dealing here with a case of chemical separation of two volatile constituents; separations of volatile constituents are sometimes effected by physical methods such as fractional condensation. Evidently it is easy to arrange matters so that water and carbon dioxide can be determined simultaneously. Such a procedure finds an important application in the elementary analysis of organic compounds, in which the sample is burned in a stream of oxygen and the water and carbon dioxide formed from the oxidation of hydrogen and carbon respectively are absorbed separately in an appropriate absorption train.

(2) *Indirect (difference) methods.* Here the weight of the residue remaining after the volatilization of a constituent is determined, and the amount of the constituent sought (which may either be volatilized or remain alone in the residue) is found from the change in weight. The method is very simple but not often applicable, since more than one volatile substance may be present or the sample may undergo chemical changes leading to change in weight of the residue (oxidation, for example). As a simple illustration of the method there may be taken the case in which it is desired to

find the amount of a dissolved salt (or salts) in an aqueous solution. This can be done very simply by evaporating the water, drying the residue at a suitable temperature, and weighing.

The method is of great practical importance in the indirect determination of water (p. 299). If the sample does not decompose on heating, its water content can be determined by heating a weighed sample to a sufficiently high temperature to expel all the water and then weighing the residue. If the substance decomposes and gives off volatile products at the temperature required to expel the water, it is sometimes possible to add to the weighed sample a weighed amount of a nonvolatile solid which combines with and retains the volatile decomposition products.

Sometimes a nonvolatile acid oxide can be added to a salt of a volatile acid to expel the volatile acid oxide on heating. Thus on heating potassium nitrate with silica, potassium silicate is formed and nitrogen pentoxide is volatilized:

$$2\ KNO_3 + SiO_2 \rightarrow K_2SiO_3 + N_2O_5.$$

In this case the loss in weight corresponds to the nitrogen pentoxide lost. Naturally such a method is highly unspecific, since salts of other acids can behave in the same way (sulfates give sulfur trioxide, etc.).

Salts containing radicals of volatile acids can be treated with a volatile strong acid and heated to expel the former and the excess of the latter:

$$2\ NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2\ HCl$$
$$2\ NaNO_3 + H_2SO_4 \rightarrow Na_2SO_4 + 2\ HNO_3.$$

In these examples, sodium chloride and nitrate are quantitatively transformed into sodium sulfate, so that it is possible to calculate the content of either alone in the sample from the increase (NaCl) or decrease ($NaNO_3$) in weight. Again the procedure is highly unspecific but nevertheless sometimes quite useful.

It is also possible to make use of chemical transformations in which certain constituents are converted into volatile compounds, e.g.:

$$CuO + H_2 \rightarrow Cu + H_2O$$
$$SiO_2 + 4\ HF \rightarrow SiF_4 + 2\ H_2O.$$

The latter reaction is frequently applied in determining the true weight of silica in an impure ignited residue of the latter (p. 405).

For reducing purposes, it is possible to make use of the ammonium halides as reagents in "difference" methods.[1] On heating, these salts dissociate into ammonia and the halogen acid. The ammonia dissociates in turn into nitrogen and hydrogen, the degree of dissociation increasing with the temperature:

$$NH_4Cl \rightleftarrows NH_3 + HCl$$
$$2\ NH_3 \rightleftarrows N_2 + 3\ H_2.$$

In addition the halogen acid dissociates:

$$2\ HCl \rightleftarrows H_2 + Cl_2,$$

---

[1] L. Moser and S. Marian, Ber. *59*, 1335 (1926).

the degree of dissociation decreasing in the order HI > HBr > HCl at a given temperature. At 327° the dissociation constant of the reaction is 1.5×10^{-6} for HCl, 3.5×10^{-3} for HBr, and 18.9 for HI. Potassium perchlorate can be quantitatively transformed into potassium bromide by heating to 400°–500° with an excess of ammonium bromide and repeating once or twice. After volatilization of the excess of the ammonium halide, the residue consists of pure potassium bromide. Similarly it is possible to transform potassium and sodium sulfates into the corresponding bromides.

3. *Miscellaneous methods.* Sometimes methods other than those based on precipitation or volatilization are used in gravimetric analysis, and some of these will be mentioned here. When the components of a heterogeneous mixture are to be determined, simple methods of physical separation can often be applied. Thus, to determine sediment in a natural water, the sample is filtered, and the dried residue on the filter is weighed; to determine the relative amounts of different solid phases in a mechanical mixture, a liquid of suitable density, in which one (or more) of the components floats, can be used in effecting a separation, followed by weighing of the different components. Special physical properties such as magnetic susceptibility can sometimes be used in effecting such separations. Even differences in appearance (e.g., color) can be made the basis of separation by manual means. To be sure, such methods are rarely applied but are valuable in isolated cases (cf. p. 693).

Differential solubility of the components of a mixture is also a property that finds application in gravimetric analysis. Methods based on this principle are frequently used in organic analysis but less often in inorganic analysis. The separation and determination of potassium in the presence of sodium by the extraction of the perchlorates of these metals by an organic solvent (p. 414) may be cited as an illustration. Potassium perchlorate is insoluble in the solvent used, whereas sodium perchlorate is easily soluble. Related to the extraction processes, of which the preceding illustration is an example, are the partition processes, in which a solution of the sample is shaken with an immiscible liquid which dissolves out one constituent but not the others (cf. p. 88).

All these methods of separation can, of course, be used preparatory to the analysis of the sample by methods other than the gravimetric.

Precipitation analysis.

We return now to the subject of precipitation processes, for these, on account of their importance, deserve further discussion.

Precipitation forms. The choice of a precipitant for a given constituent rests upon a number of factors. First of all, the precipitation form must be so slightly soluble that the precipitation can be made quantitative.[1] Then, the precipitant should, as far as possible, be specific, i.e., the other constituents present in the solution should not yield slightly soluble precipitates with the reagent, nor should they interfere with the formation of the precipitate. The precipitate of the constituent in question should not tend to be appreciably contaminated by soluble substances in the solution (see Chapter VIII regarding the phenomena of *coprecipitation*). Finally, it should be easy to filter and wash the precipitate and to prepare it for weighing.

---

[1] A macroprecipitation, or other operation, may be said to be *quantitative* when the loss of substance in the operation does not exceed *ca.* 0.1 mg., the ordinary limit of sensitivity of the analytical balance.

It is comparatively rare to find all these desiderata combined in a single precipitation form. Precipitation reagents are quite commonly lacking in the property of specificity. For this reason it is very often necessary to separate the constituent whose amount is desired from the other constituents of the sample before the former can be precipitated in pure form. (The subject of separations is considered in Chapter VI.) If the separation is made by precipitation of the constituent sought, it is sometimes necessary to dissolve the *separation form* in a suitable liquid and to reprecipitate the constituent in a form which is suitable for weighing or can be made so. Conversely, the interfering constituents can be precipitated by a suitable reagent and the desired constituent left in solution to be precipitated in another form. Interferences due to coprecipitation may require the removal of the disturbing foreign substances, or reprecipitations (p. 119). Sometimes regulation of the conditions of precipitation may permit the presence of the foreign substances during precipitation. Occasionally, when exact results are desired, corrections can be applied to the weight of the dried or ignited precipitate by determining the small amount of coprecipitated (or precipitated) foreign substance and deducting the latter.

Weighing forms. Very frequently a constituent is not weighed in the form in which it is precipitated, and this for a number of reasons. For instance, the precipitation form may be of indefinite composition. Thus ferric iron is often precipitated as hydrous ferric oxide, $Fe_2O_3 \cdot x\,H_2O$; but it is never weighed as such, because this compound after drying at room temperature or 100° contains an indefinite amount of water, depending upon the exact conditions under which it has been precipitated and dried. It is, however, a very simple matter to ignite[1] the hydrous oxide to convert it into the anhydrous form, Fe_2O_3, and so weigh it. The weighing of any precipitation form after drying at room temperature or at 100° is a procedure to be looked upon with suspicion, because a precipitate so dried may still contain water held by adsorption or inclusion (p. 118). This is not to say that certain precipitation forms may not be weighed after drying in this manner, because much depends upon the precipitate in question, but the matter must always be put to critical test. As we shall see later, many substances, especially when in the finely divided condition, retain water tenaciously and can be rendered water-free only by heating at rather high temperatures — hence the frequency with which ignition is performed as a preparatory step to weighing. It is desirable, on the one hand, that the precipitation form be decomposed or transformed [1] into the weighing form at a relatively low temperature and, on the other hand, that the latter be stable (nondecomposable and nonvolatile) at high temperatures so that the conversion can easily be effected by the usual heating appliances of the laboratory without a critical control of temperature. Moreover, the ignited residue should not be appreciably hygroscopic. Other things being equal, a weighing form will be better for the purpose the greater its molecular weight or, more exactly expressed, the larger the ratio of the weight of the substance weighed to that of the constituent being determined.

---

[1] As used in analytical chemistry, the term *ignition* means heating at a high or moderately high temperature.

It may be mentioned here that an advantage of gravimetric over volumetric analysis is that the ignited residue can be examined, after weighing, for foreign substances that might be present, and corrections applied if necessary.[2]

Calculations of gravimetric analysis.

The computations of gravimetric analysis are very simple. Generally it is desired to find the *weight percentage* of a given constituent in a sample, and then the following formula applies:

$$P = \frac{w}{W} \times 100,$$

where P = percentage of the constituent sought,
w = weight of the constituent,
W = weight of the sample.

If the constituent is weighed in the form in which the percentage is to be expressed, it is only necessary to substitute the weight of the dried or ignited residue for w in the above equation. Usually, however, the constituent is weighed in the form of a compound which contains it in a known constant amount, this practice dating back to T. Bergman (1735–1784). Then it is necessary to find w from the weight of the dried or ignited precipitate, w', by making use of the formula:

---

[1] In some cases the precipitation form is converted into a suitable weighing form by treatment with a suitable reagent, the excess of which is then volatilized. Cf weighing calcium as the sulfate, p. 354.

[2] When the amount of precipitate is very small, it is well to establish its identity qualitatively to be sure that the substance weighed is actually what it is supposed to be and not an entirely different substance.

$$w = Fw'$$

in which F (variously called the chemical factor, conversion factor, gravimetric factor, and calculation factor) is a ratio which represents the weight of w that would be given by a unit weight of w' if the substance weighed were appropriately treated. Otherwise expressed, F is the numerical value of the ratio of a gram equivalent of the constituent sought to a gram equivalent of the compound weighed. Thus in determining chlorine as chloride by weighing the silver chloride obtained by treating the solution of the sample with an excess of silver nitrate, the weight of chlorine corresponding to the weight of dry silver chloride found is obtained by making use of the factor:

$$F_{\frac{\mathrm{Cl}}{\mathrm{AgCl}}} = \frac{\mathrm{Cl}}{\mathrm{AgCl}} = \frac{35.46}{143.34} = 0.2474.$$

Illustration: A 0.2501 g. sample of a soluble chloride gave a precipitate of silver chloride weighing 0.5009 g. What is the percentage of chlorine in the sample?

$$\textit{Ans.}\ \ P = \frac{F \times w' \times 100}{W} = \frac{0.2474 \times 0.5009 \times 100}{0.2501} = 49.55\%\ \mathrm{Cl}.$$

It should be noted that in the ratio expressing the chemical factor, the formula of the substance sought occurs in the numerator and that of the substance weighed occurs in the denominator. It must be realized that since the chemical factor expresses the ratio of two substances which are equivalent to one another, the same number of atoms of the constituent concerned must appear in numerator and denominator. Thus in calculating the weight of iron from the weight of an ignited ferric oxide residue, the factor is: $\frac{2\ \mathrm{Fe}}{\mathrm{Fe_2O_3}}$. The following examples should make the principle clear:

Substance Weighed	Substance Sought	Factor
$Mg_2P_2O_7$	MgO	$\frac{2\ \mathrm{MgO}}{\mathrm{Mg_2P_2O_7}}$
$Mg_2P_2O_7$	P_2O_5	$\frac{\mathrm{P_2O_5}}{\mathrm{Mg_2P_2O_7}}$
Fe_2O_3	Fe_3O_4	$\frac{2\ \mathrm{Fe_3O_4}}{3\ \mathrm{Fe_2O_3}}$
$BaSO_4$	$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24\ H_2O$	$\frac{\mathrm{K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24\ H_2O}}{4\ \mathrm{BaSO_4}}$

The constituent sought need not be present in the substance weighed, so long as the stoichiometric relation between the two is known. Thus it is possible to determine the amount of potassium in a solution of pure potassium chloride by determining the weight of silver chloride yielded by the solution, since the weight relation between potassium and silver chloride is fixed. In this case the factor is accordingly $\frac{\mathrm{K}}{\mathrm{AgCl}}$. No matter how many the intermediate compounds in a series of stoichiometric reactions, only the first and last need be considered in setting up the calculation factor.

Indirect analysis. There are various types of indirect analyses, but they all have the common feature that all the constituents being determined are not isolated in a pure form and weighed. Thus it is possible to obtain the weight of the sum of n constituents, then determine $(n-1)$ of them by isolation (separation), and finally find the remaining one by difference. Or all the constituents (usually limited to the case in which only two are present) may be determined indirectly. For example, the amounts of two substances may be determined from the change in weight that a known amount of the mixture, composed only of these, undergoes when transformed into two other substances which differ in molecular weight not only between themselves but from the original ones as well. In any case it must be possible to set up as many independent simultaneous equations connecting the quantities of the substances involved as there are substances to be determined. The relations expressed in these equations are the stoichiometric ones. For example — to take an illustration which is often given — it is possible to determine the amount of sodium and potassium chloride respectively in a pure mixture of the two by obtaining first the weight of the mixture and then the weight of silver chloride which the sample yields.

Let a = weight of sodium and potassium chlorides,
b = weight of silver chloride,
x = weight of sodium chloride,
y = weight of potassium chloride.

Then

$$x + y = a$$

$$\frac{\mathrm{AgCl}}{\mathrm{NaCl}}\,x + \frac{\mathrm{AgCl}}{\mathrm{KCl}}\,y = b$$

$$2.452\,x + 1.923\,(a - x) = b$$

$$x = 1.890\,b - 3.635\,a.$$

Since a and b are known, x (and y) can be calculated.

Indirect methods must be used with caution because they usually cannot yield accurate results. A small error in weighing is generally multiplied many fold in the result. An inspection of the above equation shows that an error of 0.1 mg. in obtaining the weight of the mixed chlorides produces an error of nearly 0.4 mg. in the sodium chloride found (see p. 292).

PROBLEMS

1. Write the chemical factors for the following:

	Weighed	Sought
(a)	Al_2O_3	Al
(b)	CaF_2	AlF_3
(c)	$Mn_2P_2O_7$	Mn_2O_3
(d)	$CaCO_3$	$Ca(HCO_3)_2$
(e)	Pt	KCl ($KCl \rightarrow K_2PtCl_6 \rightarrow Pt$)
(f)	$PbMoO_4$	P_2O_5 ($P_2O_5 \rightarrow (NH_4)_3PO_4 \cdot 12\,MoO_3 \rightarrow PbMoO_4$)

2. 1.000 g. of an oxalic acid sample was precipitated with an excess of calcium chloride and the washed precipitate ignited to calcium oxide. The residue weighed 0.4402 g. Calculate the percentage of $H_2C_2O_4$ in the sample.

Ans. 70.68 per cent.

3. A 0.7500 g. sample of a soluble sulfate containing 0.50 per cent of moisture yielded 1.044 g. of $BaSO_4$. What is the percentage of S in the sample on (a) the moist basis, (b) the dry basis? *Ans.* (a) 19.12 per cent; (b) 19.22 per cent.

4. 25.00 ml. of a solution of barium chloride containing no other substance gave a dried precipitate of silver chloride weighing 0.3408 g. Calculate:

(a) The weight of $BaCl_2$ in 1 liter of the solution.
(b) The molarity of the solution.
(c) The normality of the solution as a precipitant for sulfate.
(d) The weight of K_2SO_4 precipitable by 25.00 ml. of the solution.

5. A mixture of anhydrous chlorides of sodium and potassium weighing 0.1000 g. gave 0.0155 g. of K_2PtCl_6. Calculate the percentages of K and Na in the mixture.

6. A 0.4000 g. sample of a pure anhydrous salt known to contain only sodium, boron, and oxygen yielded 0.4914 g. H_3BO_3 (by a volumetric method) and 0.2324 g. NaCl. What is the formula of the compound?

7. A mixture of NaCl and KCl weighing 0.5986 g. yielded 0.7072 g. of anhydrous Na_2SO_4 and K_2SO_4 when treated with sulfuric acid. Calculate the percentages of NaCl and KCl. If a weighing error of + 0.2 mg. were made in finding the weight of the mixed sulfates, what would be the resulting error in the percentages of NaCl and of KCl?

8. If 10.00 ml. of sulfuric acid solution of density 1.010 yield a pure barium sulfate precipitate weighing 0.3780 g., what is the percentage by weight of H_2SO_4 in the solution, and the molarity and normality of the latter?

Ans. 1.572 per cent; 0.1619 *M*; 0.3238 *N*.

THEORETICAL PART

CHAPTER IV

THE MASS–ACTION LAW

DISSOCIATION OF ELECTROLYTES. HYDROGEN–ION CONCENTRATION OF VARIOUS SOLUTIONS

Equilibrium in a reversible reaction. The mass-action law.

When two substances, A and B, react with each other and there is no further change in the relative masses of the two substances, *equilibrium* has been reached. When the reaction products, C and D, can react with each other to form A and B, the reaction is said to be *reversible* and is generally written in the following form:

$$A + B \rightleftarrows C + D.$$

In quantitative analysis we are usually dealing with reversible reactions in which homogeneous equilibrium is reached within a very short time. The equilibrium itself is not static but is dynamic, which means that under equilibrium conditions A and B still react to form C and D, and the latter react to give A and B again; in a given period of time the quantity of A and B disappearing by interaction is equal to that formed as a result of the reaction between C and D. In other words, when equilibrium has been reached, the velocity of the reaction between A and B is equal to that between C and D. The speed of the reactions is expressed by the *Law of Mass Action*, first clearly stated by Guldberg and Waage.[1] *The rate of reaction is proportional to the active concentrations of the reacting substances, each raised to the power numerically equal to the number of molecules appearing in the balanced equation.*

In this text concentrations will generally be expressed in moles per liter instead of in active masses or activities (see, however, p. 53). Molar concentrations are denoted by a chemical formula or symbol enclosed in brackets [ ]. According to the mass-action law the velocity, v_1, of the reaction between A and B in the above equation is

---

[1] C. M. Guldberg and P. Waage, J. prakt. Chem. (2) *19*, 69 (1879).

$$v_1 = k_1[A][B],$$

and that between C and D is

$$v_2 = k_2[C][D].$$

k_1 and k_2 are constants. When equilibrium is reached, $v_1 = v_2$, and

$$k_1[A][B] = k_2[C][D]$$

or

$$\frac{[C][D]}{[A][B]} = \frac{k_1}{k_2} = K\,(t = \text{const.}).$$

If we consider the reaction between 2 A and B:

$$2\,A + B \rightleftarrows C + D$$

or

$$A + A + B \rightleftarrows C + D,$$

it is easily shown that

$$\frac{[C][D]}{[A]^2[B]} = K\,(t = \text{const.}).$$

The equilibrium constant for the general reversible reaction:

$$aA + bB + cC + \cdots \rightleftarrows pP + qQ + rR + \cdots$$

is

$$K = \frac{[P]^p[Q]^q[R]^r \cdots}{[A]^a[B]^b[C]^c \cdots}.$$

K is called the *equilibrium constant* (constant at a *given temperature*).

It should be understood that there is no relation between the rate at which a reaction reaches equilibrium and the magnitude of its equilibrium constant. The speed of most reactions increases rapidly with increasing temperature (usually more than twofold for every increase of 10° C.) and is also affected by the presence of certain substances which have a specific effect. Such substances are called *positive catalysts* if they *increase* the rate of reaction.

Positive catalysts are used in analysis to increase the speed of slow quantitative reactions. Some oxidation-reduction reactions employed in volumetric analysis proceed rather slowly. This, for example, is the case with the reaction between hydrogen peroxide and iodide in acid medium, or bromate with iodide in acid medium:

$$H_2O_2 + 2\,H^+ + 2\,I^- \rightarrow 2\,H_2O + I_2$$
$$BrO_3^- + 6\,H^+ + 6\,I^- \rightarrow Br^- + 3\,I_2 + 3\,H_2O.$$

The addition of a trace of molybdate catalyzes the reactions so strongly that the titration of iodine can be made without waiting.

Theorem of Le Chatelier-van't Hoff. This theorem may be stated as follows: *Any alteration in the factors which determine chemical* *equilibrium causes the equilibrium to become displaced in such a way as to oppose as far as possible the effect of the alteration.* An increase in the temperature of a system in equilibrium displaces the equilibrium in such a way that heat is absorbed. For example, the heat of neutralization of a strong acid with a strong base is determined by the following reaction:

$$H^+ + OH^- \rightleftarrows H_2O + 13{,}900 \text{ calories.}$$

The formation of water takes place with the evolution of much heat. According to the above rule the equilibrium will be displaced from the right to the left by a rise in temperature or, in other words, *the dissociation of water into hydrogen and hydroxyl ions increases with increasing temperature.*

Strong and weak electrolytes.

Electrolytes are substances which dissociate more or less completely into ions when dissolved in water. According to modern electrochemical theories a distinction may be made between *strong* and *weak* electrolytes. Strong electrolytes when dissolved in water are virtually completely dissociated into ions, whereas in solutions of weak electrolytes, ions and undissociated molecules of the electrolyte are both present.

To the group of strong electrolytes the following belong:

- *Various inorganic acids:* perchloric, nitric, hydrochloric, hydrobromic, and hydriodic acids.
- *The hydroxides of the alkalies, of silver, and the alkaline earths.*
- *Almost all salts* (exceptions: the halides, cyanides, and thiocyanates of mercury, cadmium, zinc, and a few others).

To the group of the weak electrolytes belong:

- *Some inorganic acids:* e.g., phosphoric, sulfurous, boric, and carbonic acids.
- *Some inorganic hydroxides* such as ammonium hydroxide, most divalent and trivalent metal hydroxides, hydrazine, and hydroxylamine.
- *Virtually all the organic acids* (with the exception of sulfonic acids).
- *Virtually all the organic bases.*

Ion concentrations in solutions of strong electrolytes.

Since strong electrolytes are completely ionized in aqueous solutions, the ion concentrations are directly found from the molecular concentration of the solution.

Examples:

$$HCl \rightarrow H^+ + Cl^-.$$

In a 0.1 *M* solution of hydrochloric acid the hydrogen-ion concentration $[H^+]$[1] is equal to the chloride-ion concentration $[Cl^-]$, and both are equal to 0.1 or 10^{-1}.

$$NaOH \rightarrow Na^+ + OH^-.$$

In 0.01 *M* NaOH: $[Na^+] = [OH^-] = 0.01 = 10^{-2}$.

$$BaCl_2 \rightarrow Ba^{++} + 2\,Cl^-.$$

In 0.01 *M* barium chloride solution: $[Ba^{++}] = 0.01 = 10^{-2}$

$$[Cl^-] = 0.02 = 2 \times 10^{-2}.$$

$$Ag_2SO_4 \rightarrow 2\,Ag^+ + SO_4^=.$$

In 0.001 *M* silver sulfate solution:

$$[Ag^+] = 0.002 = 2 \times 10^{-3}$$
$$[SO_4^=] = 0.001 = 10^{-3}.$$

The dissociation of weak electrolytes.

In aqueous solutions a weak acid, HA, is only partly dissociated into hydrogen ions and anions, and the remaining part of the acid is present in the undissociated state:

$$HA \rightleftarrows H^+ + A^-. \tag{1}$$

The reaction is reversible, and equilibrium is attained instantaneously. Therefore, in any solution of a weak electrolyte the mass-action law may be applied:

$$\frac{[H^+][A^-]}{[HA]} = K_a \text{ (at constant temperature).} \tag{2}$$

The equilibrium constant K_a is called the *ionization constant* of the acid. In dissociating, the acid gives an equal number of hydrogen ions and anions.

Therefore $[H^+] = [A^-]$, and instead of (2) we may write:

$$\frac{[H^+]^2}{[HA]} = K_a. \tag{3}$$

If the molar concentration of the acid is c, then the concentration of the undissociated part, $[HA]$, is equal to the total concentration less the concentration of the dissociated part:

$$[HA] = c - [H^+] = c - [A^-].$$

Therefore
$$\frac{[H^+]^2}{c - [H^+]} = K_a \tag{4}$$

and[2]
$$[H^+] = -\frac{K_a}{2} + \sqrt{\frac{K_a^2}{4} + K_a c}. \tag{5}$$

---

[1] Actually no free protons (H^+) exist. In aqueous media the hydrogen ions combine completely with the solvent H_2O to form hydronium ions H_3O^+. Although in this text the symbol $[H^+]$ is used for the hydrogen-ion concentration, it should be realized that $[H_3O^+]$ is actually meant.

[2] Do not memorize these expressions but derive them whenever needed.

In many cases it will be found that $[H^+]$ is so small compared with c that $c - [H^+]$ becomes virtually equal to c. In an approximate form equation (4) may then be written:

$$[H^+]^2 = K_a c$$

$$[H^+] = \sqrt{K_a c}. \tag{6}$$

One can often use the approximate equation (6) since if $[H^+]$ is less than about 5 per cent of c, the result obtained is sufficiently accurate; if $[H^+]$ is greater than 5 per cent, the exact equation (5) should be employed. In Table I on page 37 the ionization constants of some common acids and bases are given.

Example: What is the hydrogen-ion concentration of a 0.1 M solution of an acid having an ionization constant of 10^{-5}? (For acetic acid $K_a = 1.8 \times 10^{-5}$.)

According to (6),

$$[H^+] = 10^{-3}.$$

Since $c = 10^{-1}$, $c - H^+$ is virtually equal to 10^{-1}.

(Show that it is no longer permissible to calculate the hydrogen-ion concentration with the aid of equation (6) in a 0.0001 M solution of acetic acid.)

Dibasic acids, H_2A, have two ionization constants:

$$H_2A \rightleftarrows H^+ + HA^- \tag{7}$$

$$HA^- \rightleftarrows H^+ + A^=. \tag{8}$$

$$\frac{[H^+][HA^-]}{[H_2A]} = K_1$$

$$\frac{[H^+][A^=]}{[HA^-]} = K_2.$$

K_1 is called the first, and K_2 the second, ionization constant of the acid. In the calculation of the hydrogen-ion concentration in a solution of a dibasic acid, one can usually neglect [1] the second dissociation (eq. 8), because the latter is repressed by the first dissociation according to equation (7). Therefore equation (5) or (6) can be applied, in which K_a is put equal to K_1.

It is now a simple matter to calculate the hydroxyl-ion concentration in a solution of a weak base BOH:

$$BOH \rightleftarrows B^+ + OH^-$$

$$\frac{[B^+][OH^-]}{[BOH]} = K_b. \tag{9}$$

K_b denotes the ionization constant of the weak base.

$$[OH^-] = -\frac{K_b}{2} + \sqrt{\frac{K_b^2}{4} + K_b c}$$

or in an approximate form:

$$[OH^-] = \sqrt{K_b c}.$$

---

[1] For a more detailed discussion see I. M. Kolthoff and H. A. Laitinen, *The Determination of pH. Electrometric Titrations*, 2d ed., John Wiley and Sons, New York, 1941.

TABLE I. IONIZATION CONSTANTS OF SOME ACIDS AND BASES AT 25°

INORGANIC ACIDS	K_a	$-\log K_a = pK_a$
Boric	5.5×10^{-10}	9.26
Carbonic K_1	3.5×10^{-7}	6.46
K_2	5×10^{-11}	10.30
Chromic K_2	1.0×10^{-7}	7.00
Hydrofluoric	1.7×10^{-5}	4.77
Phosphoric K_1	7.0×10^{-3}	2.16
K_2	7×10^{-8}	7.16
K_3	4×10^{-13}	12.4
Sulfuric K_2	1.2×10^{-2}	1.92
Sulfurous K_1	1.7×10^{-2}	1.77
K_2	6.2×10^{-8}	7.21
Hydrogen sulfide K_1	5.7×10^{-8}	7.24
K_2	1.2×10^{-15}	14.92
ORGANIC ACIDS		
Acetic	1.8×10^{-5}	4.74
Benzoic	6.7×10^{-5}	4.17
Citric K_1	8.7×10^{-4}	3.06
K_2	1.8×10^{-5}	4.74
K_3	4.0×10^{-6}	5.40
Formic	2×10^{-4}	3.70
Hydrocyanic acid	7.2×10^{-10}	9.14
Oxalic K_1	6.5×10^{-2}	1.19
K_2	6.1×10^{-5}	4.11
Tartaric K_1	9.6×10^{-4}	3.02
K_2	2.9×10^{-5}	4.54
BASES	K_b	$-\log K_b = pK_b$
Ammonia	1.75×10^{-5}	4.76
Lead hydroxide	9.6×10^{-4}	3.02
Hydrazine	3×10^{-6}	5.52
Methylamine	4.4×10^{-4}	3.30
Aniline	4×10^{-10}	9.40
Pyridine	1.4×10^{-9}	8.85

The dissociation of water. The hydrogen-ion exponent, pH.

Water is an extremely weak electrolyte and is only very slightly dissociated into its ions:

$$H_2O \rightleftarrows H^+ + OH^-. \tag{10}$$

Application of the mass-action law yields:

$$\frac{[H^+][OH^-]}{[H_2O]} = K. \tag{11}$$

H_2O represents the molar concentration of water in water (*ca.* 55). As long as we work with dilute aqueous solutions, the concentration of the water may be considered as constant. It is evident then that instead of (11) we may write at constant temperature:

$$[H^+][OH^-] = K[H_2O] = K_w. \qquad (12)$$

In all problems of acidity and basicity K_w is a constant of utmost importance. It is called the *ionization product* of water. Its value increases rapidly with the temperature. At 24° K_w is equal to 1×10^{-14}, at 100° to approximately 1×10^{-12}, thus being 100 times as large at 100° as at 24°. In the following discussion we shall assume that at room temperature $K_w = 10^{-14}$, although this is true only at 24°. The value of K_w increases approximately 8 per cent per degree rise in temperature. With the aid of equation (12) it is a simple matter to calculate the hydrogen-ion concentration of pure water.

From a practical viewpoint it is important to note that it is very hard to prepare entirely pure water and to keep it unchanged. The atmosphere contains 0.03 volume per cent of carbon dioxide, which is fairly readily dissolved by water, dividing itself between water and air in a ratio of 1 : 1. In other words, water in equilibrium with the air contains 0.03 volume per cent of carbon dioxide. Such a solution has a hydrogen-ion concentration about twenty times larger than that of pure water (see Problem 3 at the end of this chapter). Pure water is usually prepared by distillation from alkaline medium. If the original water contains a trace of ammonia, the latter will be carried into the distillate and will decrease the hydrogen-ion concentration of the latter (see Problem 2 at the end of this chapter). If pure water is kept in ordinary glass containers, alkali from the glass will be dissolved, and the hydrogen-ion concentration will decrease. When exposed to the laboratory atmosphere, water quickly absorbs acid and alkaline fumes. Hence pure water must be handled with great care and must never be exposed to the atmosphere.

From equation (10) it follows that in the dissociation of water as many hydrogen as hydroxyl ions are formed. Therefore in pure water it is found that $[H^+] = [OH^-]$, and

$$[H^+]^2 = [OH^-]^2 = 10^{-14}$$

$$[H^+] = [OH^-] = 10^{-7} \quad \text{(room temperature).}$$

Pure water contains one ten-millionth of a gram of hydrogen ions and seventeen ten-millionths of a gram of hydroxyl ions per liter.

Any aqueous solution contains both hydrogen and hydroxyl ions. If by the addition of hydrogen ions (an acid) $[H^+]$ is made larger than 10^{-7}, $[OH^-]$ will become smaller; in basic solutions $[OH^-]$ will be greater than 10^{-7} and greater than $[H^+]$. The product of $[H^+]$ and $[OH^-]$ always remains constant.

$$[H^+] = \frac{K_w}{[OH^-]} \quad \text{and}$$

$$[OH^-] = \frac{K_w}{[H^+]}.$$

ILLUSTRATION: What is $[H^+]$ in 0.01 N sodium hydroxide?

$$[OH^-] = 10^{-2}; \quad \text{therefore} \quad [H^+] = \frac{10^{-14}}{10^{-2}} = 10^{-12}.$$

For various reasons it is often advantageous to express ion concentrations in terms of their negative logarithms to the base 10. This negative logarithm is usually called the *ion exponent* and is designated by the symbol p.

Thus pH designates the *hydrogen-ion exponent* and is equal to the *negative* logarithm of the hydrogen-ion concentration:

$$\text{pH} = -\log [H^+].$$

Similarly,

$$\text{pOH} = -\log [OH^-].$$

pOH is the hydroxyl-ion exponent. The relation between the ion concentration and the ion exponent is simply expressed algebraically:

$$\text{pH} = \log \frac{1}{[H^+]} = -\log [H^+]$$

$$[H^+] = 10^{-\text{pH}}.$$

EXAMPLES:

(1) $[H^+] = 5 \times 10^{-3}$. What is the pH?[1]

$$\text{pH} = -\log (5 \times 10^{-3}) = (-\log 5) + 3 = -0.7 + 3 = 2.3.$$

(2) pH = 4.4. What is $[H^+]$?

$$[H^+] = 10^{-4.4} = 10^{-5} \times 10^{+0.6} = x \times 10^{-5}$$

$$10^{+0.6} = x$$

$$\log x = 0.6$$

$$x = 3.98$$

$$[H^+] = 3.98 \times 10^{-5}.$$

Now we can write equation (12) in terms of negative logarithms:

$$-\log [H^+] + (-\log [OH^-]) = -\log K_w$$

or

$$\text{pH} + \text{pOH} = \text{p}K_w.$$

---

[1] Do not use more than two decimal places in the expression of pH.

pK_w denotes the negative logarithm of the ionization product of water (ionization-product exponent). At room temperature we find

$$\begin{aligned} \text{pH} + \text{pOH} &= -\log 10^{-14} = 14 \\ \text{pH} &= 14 - \text{pOH} \\ \text{pOH} &= 14 - \text{pH}. \end{aligned}$$

If $[\text{H}^+] = [\text{OH}^-] = 10^{-7}$ and pH = pOH = 7, the solution has a *neutral* reaction. If $[\text{H}^+] > 10^{-7} > [\text{OH}^-]$, or pH < 7 < pOH, the solution has an *acid reaction.* If $[\text{H}^+] < 10^{-7} < [\text{OH}^-]$, or pH > 7 > pOH, the solution has an *alkaline reaction.* It should be realized that *decreasing* pH *means increasing hydrogen-ion concentration.*

In Figure 1 the pH of various solutions is given.

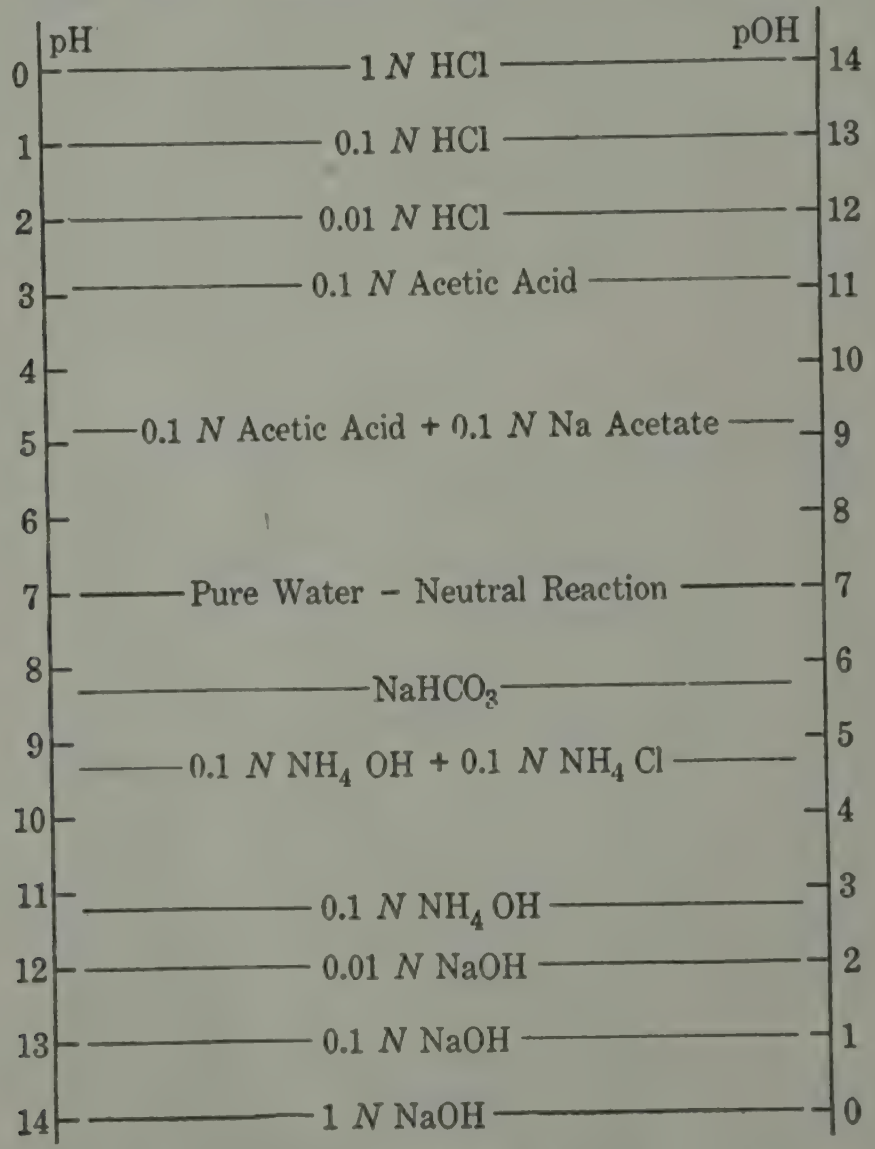

pH
pOH
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
1 N HCl
0.1 N HCl
0.01 N HCl
0.1 N Acetic Acid
0.1 N Acetic Acid + 0.1 N Na Acetate
Pure Water - Neutral Reaction
NaHCO₃
0.1 N NH₄ OH + 0.1 N NH₄ Cl
0.1 N NH₄ OH
0.01 N NaOH
0.1 N NaOH
1 N NaOH
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0

FIG. 1. pH–pOH scale at 24° ($K_w = 10^{-14}$).

Hydrolysis of salt solutions.

We have seen that pure water can split off hydrogen and hydroxyl ions. In using water as a solvent for salts, the reaction of the solution may remain neutral or may become acid or basic, depending on the properties of the salt. If the latter consists of the cation of a strong base and the anion of a strong acid, the reaction of the solvent remains *unchanged.* Such salts are called *neutral salts.* The alkali and alkaline earth salts of the halogen acids, nitric acid, perchloric acid, and sulfuric acid are examples of neutral salts.

The salt sodium chloride, being a strong electrolyte, is completely dissociated into sodium and chloride ions. Since sodium hydroxide is a strong base, sodium ions have no tendency to combine with the hydroxyl ions furnished by the water to form undissociated sodium hydroxide. Neither do the chloride ions show a tendency to combine with hydrogen ions furnished by the water. Consequently, it is found that *neutral salts do not change the reaction of the medium.*

Now let us consider the salt of a weak base and a strong acid, such as ammonium chloride. The chloride ions again do not react with the hydrogen ions. The ammonium ions on the other hand are the cations of a weak base. They have a tendency to combine with hydroxyl ions to form undissociated ammonium hydroxide. Consequently, the hydroxyl concentration of the water will be decreased and the hydrogen ion concentration increased, since the product $[H^+][OH^-]$ must remain constant:

$$NH_4Cl \rightarrow NH_4^+ + Cl^-$$

$$NH_4^+ + H_2O \rightleftarrows NH_4OH + H^+.$$

This interaction between the cation and the water is a case of *hydrolysis.* As a result of the hydrolysis a solution of a salt of a weak base and a strong acid will have an acid reaction. It is easily seen that a solution of a salt of a strong base and a weak acid will have an alkaline reaction because of hydrolysis:

$$KCN \rightarrow K^+ + CN^-$$

$$CN^- + H_2O \rightleftarrows HCN + OH^-.$$

It is of interest to calculate the hydrogen-ion concentration of a hydrolyzed salt solution. From the above qualitative considerations it is readily understood that the degree of hydrolysis of a salt of a weak base and a strong acid increases with decreasing strength or ionization constant of the base and increasing dissociation of the water (increasing temperature), and the degree of hydrolysis of the salt of a weak acid and a strong base increases with decreasing strength of the acid and increasing dissociation of the water.

Let us now derive the hydrogen-ion concentration of a solution of a salt BCl, in which B^+ is the cation of a weak base:

$$\mathrm{BCl} \rightarrow \mathrm{B}^+ + \mathrm{Cl}^-$$

$$\mathrm{B}^+ + \mathrm{H_2O} \rightleftarrows \mathrm{BOH} + \mathrm{H}^+. \tag{13}$$

The last reaction is reversible, and therefore the mass-action law can be applied at equilibrium:

$$\frac{[\mathrm{BOH}][\mathrm{H}^+]}{[\mathrm{B}^+][\mathrm{H_2O}]} = K.$$

Since the concentration of water can be considered constant, the following equation may be written instead of the preceding:

$$\frac{[\mathrm{BOH}][\mathrm{H}^+]}{[\mathrm{B}^+]} = K_{\mathrm{hydr.}} \tag{14}$$

$K_{\mathrm{hydr.}}$ is usually called the *hydrolysis constant*, and it can be shown that its magnitude is a simple function of K_b and K_w.

Multiplying numerator and denominator in equation (14) by $[\mathrm{OH}^-]$, we obtain:

$$\frac{[\mathrm{BOH}]}{[\mathrm{B}^+][\mathrm{OH}^-]}[\mathrm{H}^+][\mathrm{OH}^-] = K_{\mathrm{hydr.}} \tag{15}$$

The expression $\frac{[\mathrm{BOH}]}{[\mathrm{B}^+][\mathrm{OH}^-]}$ is the reciprocal of that in equation (9) and is equal to $\frac{1}{K_b}$, and $[\mathrm{H}^+][\mathrm{OH}^-] = K_w$; therefore,

$$\frac{[\mathrm{BOH}]}{[\mathrm{B}^+][\mathrm{OH}^-]}[\mathrm{H}^+][\mathrm{OH}^-] = \frac{K_w}{K_b} = K_{\mathrm{hydr.}} \tag{16}$$

Equation (13) shows that an equal number of undissociated molecules, BOH, and hydrogen ions are formed by the hydrolysis. Therefore, in the hydrolyzed salt solution:

$$[\mathrm{BOH}] = [\mathrm{H}^+]. \tag{17}$$

Since the salt itself is a strong electrolyte, it is completely dissociated into its ions. If c represents the total concentration of the salt,

$$[\mathrm{B}^+] = [\mathrm{Cl}^-] = c. \tag{18}$$

(Actually $[\mathrm{B}^+] = c - [\mathrm{BOH}]$; but the difference, as a rule, is so small that it may be neglected.)

From equations (14), (16), (17), and (18) it is found that

$$\frac{[\mathrm{BOH}][\mathrm{H}^+]}{[\mathrm{B}^+]} = \frac{[\mathrm{H}^+]^2}{c} = \frac{K_w}{K_b}$$

and

$$[\mathrm{H}^+] = \sqrt{\frac{K_w}{K_b}c}. \tag{19}$$

Example: What is $[H^+]$ in 0.1 N ammonium chloride solution at 24° if K_b is equal to 10^{-5}?

$$[H^+] = \sqrt{\frac{10^{-14}\,0.1}{10^{-5}}} = 10^{-5}.$$

For the solution of a salt of a weak acid and a strong base, KA, an expression analogous to (19) can be derived:

$$KA \rightarrow K^+ + A^-$$

$$A^- + H_2O \rightleftarrows HA + OH^-$$

$$\frac{[HA][OH^-]}{[A^-]} = K_{\text{hydr.}} = \frac{K_w}{K_a} \tag{20}$$

$$\frac{[OH^-]^2}{c} = \frac{K_w}{K_a}$$

$$[OH^-] = \sqrt{\frac{K_w}{K_a}\,c} \tag{21}$$

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{K_w}{\sqrt{\frac{K_w}{K_a}\,c}} = \sqrt{\frac{K_w K_a}{c}}. \tag{22}$$

The reaction in a mixture of a weak acid and its salt or a weak base and its salt. Buffer action.

In any solution containing a weak acid, HA, the equilibrium is determined by the magnitude of the ionization constant:

$$\frac{[H^+][A^-]}{[HA]} = K_a$$

and

$$[H^+] = \frac{[HA]}{[A^-]}\,K_a. \tag{23}$$

Considering now a mixture of a weak acid and its salt, we must realize that the salt, KA, is a strong electrolyte and that the concentration of A^- ions sent into solution by the salt is practically equal to the molecular concentration c_s of the salt. The salt represses the dissociation of the acid, HA, because it furnishes the common ion A^-.

In most cases this repression of the dissociation is so great that we can consider all of the acid present to be in the undissociated form. If the analytical concentration of the acid is c_a, we find then that $[HA] = c_a$ and $[A^-] = c_s$. Introduction of these values in equation (23) gives the hydrogen-ion concentration of a mixture of a weak acid and its salt:

$$[H^+] = \frac{c_a}{c_s}\,K_a. \tag{24}$$

Actually this is only an approximate expression; it will, however, be used in this text. In a mixture of a weak acid and its salt having an acid reaction, the hydrogen ions are furnished by dissociation of the acid, and an equal amount of A^- ions is formed. Exactly expressed then, $[HA] = c_a - [H^+]$, and $[A^-] = c_s + [H^+]$. Introducing these expressions in equation (23), it is found that

$$[H^+] = \frac{c_a - [H^+]}{c_s + [H^+]} K_a. \tag{24a}$$

This is a quadratic equation which can be easily solved for $[H^+]$.

A mixture of a very weak acid containing an excess of the salt may have an alkaline reaction owing to the hydrolysis of the salt:

$$A^- + H_2O \rightleftarrows HA + OH^-.$$

This hydrolysis is repressed by the presence of HA in the mixture. Still, as a result of the hydrolysis, it is easily seen that

$$[HA] = c_a + [OH]^- = c_a + \frac{K_w}{[H^+]}$$

and

$$[A^-] = c_s - [OH^-] = c_s - \frac{K_w}{[H^+]}.$$

Introducing these results in equation (23), it is found that:

$$[H^+] = \frac{c_a + \dfrac{K_w}{[H^+]}}{c_s - \dfrac{K_w}{[H^+]}} K_a \tag{24b}$$

This again is a simple quadratic equation which can be easily solved for $[H^+]$.

By analogous reasoning it is found that in a mixture of a weak base and its salt:

$$\frac{[B^+][OH^-]}{[BOH]} = K_b$$

$$[OH^-] = \frac{[BOH]}{[B^+]} K_b = \frac{c_b}{c_s} K_b$$

$$[H^+] = \frac{K_w c_s}{K_b c_b}. \tag{25}$$

Here c_s denotes the concentration of the salt of the weak base and c_b that of the weak base itself.

Mixtures of weak acids and their salts or of weak bases and their salts are called *buffer solutions since they resist a change in hydrogen-ion concentration upon addition of slight amounts of acids or bases.* The pH of such buffer mixtures hardly changes on dilution.

Suppose, for example, that we have a mixture of acetic acid and sodium acetate in which $c_a = c_s = 0.1$. The hydrogen-ion concentration of this mixture is:

$$[H^+] = \frac{c_a}{c_s} K_a = K_a = 1.8 \times 10^{-5}$$

$$pH = 4.74.$$

Now let an amount of base equivalent to 1 ml. of 0.1 *N* sodium hydroxide be added to 100 ml. of this mixture. The result is that an equivalent amount of acetic acid is neutralized and sodium acetate is formed. Therefore [HA] becomes $0.1 - 0.001 = 0.099$, $[A^-] = 0.1 + 0.001 = 0.101$, and

$$[H^+] = \frac{0.099}{0.101} K_a = 0.98\, K_a = 1.76 \times 10^{-5}$$

$$\text{pH} = 4.75.$$

Therefore the addition of this amount of base hardly changes the pH of the solution.

Buffer solutions play a very important rôle in the colorimetric determination of pH with the aid of indicators. Use is often made in analytical chemistry of the buffer action of mixtures of weak acids and their salts or of weak bases and their salts. Precipitations must often be made in a certain range of pH values. The pH is then adjusted by the addition of a suitable buffer mixture. In the precipitation of aluminum with ammonia, one is confronted with the difficulty that hydrous aluminum oxide dissolves partially in an excess of ammonia owing to the formation of aluminate. The solubility of the oxide increases linearly with the hydroxyl-ion concentration. Addition of a suitable amount of ammonium chloride decreases the hydroxyl-ion concentration to such an extent that the solubility becomes negligibly small. Another advantageous application of the buffer action of the ammonia-ammonium salt system is made in separations in which magnesium hydroxide must be kept in solution. This case will be discussed more in detail in the chapter on "Separations," where other examples are also given.

In many cases the acidity of a strongly acid solution must be decreased before a certain operation can be carried out. This is often done by the addition of an adequate quantity of sodium acetate or sometimes by adding sodium bicarbonate.

In the latter case we have the buffer system $H_2CO_3 + NaHCO_3$:

$$[H^+] = \frac{[H_2CO_3]}{[HCO_3^-]} \cdot K_1 = \frac{[H_2CO_3]}{[HCO_3^-]} \times 3 \times 10^{-7}.$$

Carbonic acid is relatively slightly soluble in water. Its saturated solution (which loses carbon dioxide fairly rapidly on exposure to the air) has a concentration of about 5×10^{-2} molar. In solutions saturated with carbon dioxide it is found that:

$$[H^+] = \frac{1}{[HCO_3^-]} \times 5 \times 10^{-2} \times 3 \times 10^{-7} = \frac{1}{[HCO_3^-]} \times 1.5 \times 10^{-8}.$$

If the sodium bicarbonate concentration were 0.15 N, we would find:

$$[H^+] = \frac{1.5 \times 10^{-8}}{1.5 \times 10^{-1}} = 10^{-7} \text{ and a pH of 7.}$$

Therefore mixtures of sodium bicarbonate and acid will have a reaction in the neighborhood of the neutral point. A very useful application of this system is made in the titration of arsenious oxide with iodine:

$$As_2O_3 + 2\,I_2 + 2\,H_2O \rightleftarrows As_2O_5 + 4\,H^+ + 4\,I^-.$$

This reaction is reversible; in neutral solution it runs quantitatively from left to right, in strongly acid medium quantitatively from right to left. Therefore in the titration of the arsenic trioxide an excess of sodium bicarbonate is added to the acid solution before titration with iodine.

PROBLEMS

1. Calculate the hydrogen-ion concentration and the pH of the following solutions: (a) 0.01 M hydrochloric acid; (b) 0.1 M acetic acid; (c) 0.001 M acetic acid; (d) 1 M ammonia; (e) 0.01 M ammonia; (f) 0.1 M sodium hydroxide. List of ionization constants is given on p. 37. $K_w = 10^{-14}$.

Ans. (a) $[H^+] = 1.0 \times 10^{-2}$; pH = 2.00;
(b) $[H^+] = 1.3 \times 10^{-3}$; pH = 2.88;
(c) $[H^+] = 1.2 \times 10^{-4}$; pH = 3.91;
(d) $[H^+] = 2.4 \times 10^{-12}$; pH = 11.62;
(e) $[H^+] = 2.5 \times 10^{-11}$; pH = 10.61;
(f) $[H^+] = 1.0 \times 10^{-13}$; pH = 13.00.

2. A sample of water contains 0.85 mg. of ammonia per liter. Calculate the pH if ammonia is the only contaminant. $K_b = 1.8 \times 10^{-5}$. *Ans.* pH = 9.35.

3. Distilled water in equilibrium with the air contains carbon dioxide, corresponding to a molar concentration of 1.35×10^{-5}. Calculate the pH of this water, given K_1 of $H_2CO_3 = 3 \times 10^{-7}$. *Ans.* pH = 5.73.

4. Calculate $[OH^-]$ and pH of a solution of 0.1 M ammonia (a) at 25°, (b) at 100°. $K_w = 10^{-14}$ at 25° and 10^{-12} at 100°. $K_b = 1.8 \times 10^{-5}$ at 25° and at 100°.

Ans. (a) $[OH^-] = 1.3 \times 10^{-3}$, pH = 11.13;
(b) $[OH^-] = 1.3 \times 10^{-3}$; pH = 9.13.

5. Calculate the pH of the following solutions: (a) 1 M sodium metaborate (NaH_2BO_3); (b) 0.01 M sodium metaborate; (c) 0.1 M anilinium perchlorate. $K_{H_3BO_3} = 5.5 \times 10^{-10}$; $K_{aniline} = 4 \times 10^{-10}$.

Ans. (a) pH = 11.63; (b) pH = 10.62; (c) pH = 2.80.

6. Calculate the pH of the following solutions containing:
(a) 0.05 mole acetic acid and 0.05 mole sodium acetate per liter.
(b) 0.05 mole acetic acid and 0.005 mole sodium acetate per liter.
(c) 0.005 mole acetic acid and 0.05 mole sodium acetate per liter.
(d) 0.005 mole acetic acid and 0.5 mole sodium acetate per liter.
$K_a = 1.8 \times 10^{-5}$.

Ans. (a) pH = 4.74; (b) pH = 3.74; (c) pH = 5.74; (d) pH = 6.74.

7. Calculate the pH of the following solutions containing:
(a) 0.1 mole NH_4OH and 0.1 mole NH_4Cl per liter.
(b) 0.01 mole NH_4OH and 0.1 mole NH_4Cl per liter.

(c) 0.1 mole NH_4OH and 0.01 mole NH_4Cl per liter.
$K_b = 1.8 \times 10^{-5}$.

Ans. (a) pH = 9.26; (b) pH = 8.26; (c) pH = 10.26.

8. To 100 ml. of 0.5 *N* sodium hydroxide are added 5.35 g. of ammonium chloride. Calculate the pH, assuming that the volume is not changed by the addition of the salt. *Ans.* pH = 9.26.

9. It is desired to change the pH of 100 ml. of 0.1 *N* hydrochloric acid solution from 1 to 4.4 by the addition of sodium acetate. How much of the solid salt $CH_3COONa \cdot 3\ H_2O$ must be added? *Ans.* 1.98 g.

CHAPTER V

SOLUBILITY AND SOLUBILITY PRODUCT

Solubility product.

In precipitation analysis we are usually dealing with slightly soluble salts which behave like strong electrolytes. According to the definition of strong electrolytes, saturated solutions of such slightly soluble salts are practically completely ionized into the component ions. Let us consider a solution of a slightly soluble salt, BA, which is in equilibrium with the solid phase BA:

$$\underset{(solid)}{\mathrm{BA}} \rightleftarrows \underset{(solution)}{\mathrm{B^+ + A^-}}.$$

The reaction is represented as a reversible one because it can be shown experimentally (with the aid of radioactive indicators) that at equilibrium as much BA goes into solution (reaction from left to right) as is formed in the same time by combination of B^+ and A^- (reaction from right to left). Therefore, when equilibrium is attained, the law of mass action gives the following relation:

$$\frac{[\mathrm{B^+}][\mathrm{A^-}]}{[\mathrm{BA}]} = K. \tag{1}$$

$[B^+]$ and $[A^-]$ represent the concentrations (or better the active masses) of the B^+ and A^- ions respectively, and [BA] is the active mass of the solid BA. As long as the latter is present, its active mass in the solution will be constant and independent of the amount of solid present. Therefore instead of (1) we may write:

$$[\mathrm{B^+}][\mathrm{A^-}] = K \cdot \text{constant} = S_{BA}. \tag{2}$$

S_{BA} is a constant (if the temperature be maintained constant) and is called the *solubility product* of the salt BA.

If the difficultly soluble salt has the general formula B_mA_n, one molecule will furnish m cations and n anions:

$$\mathrm{B}_m\mathrm{A}_n \rightleftarrows m\,\mathrm{B}^{b+} + n\,\mathrm{A}^{a-}.$$

Application of the mass-action law then yields:

$$[\mathrm{B}^{b+}]^m[\mathrm{A}^{a-}]^n = S_{B_mA_n}. \tag{3}$$

Solubility and solubility product.

In a saturated solution of the slightly soluble salt, BA, in water the concentration of the B^+ ions is equal to that of the A^- ions. Since the salt is completely ionized:

$$[B^+] = [A^-] = s \tag{4}$$

if s represents the molar solubility of the salt.

From equations (2) and (4) it is easily found that in the saturated solution:

$$[B^+]^2 = [A^-]^2 = s^2 = S_{BA}$$

$$[B^+] = [A^-] = s = \sqrt{S_{BA}}. \tag{5}$$

Therefore, the solubility of the salt and the concentration of the cation and of the anion can be calculated very easily from the solubility product.

Example: The solubility product of silver chloride at 25° is approximately equal to 10^{-10}. Then the solubility s of silver chloride is $\sqrt{10^{-10}} = 10^{-5}$ mole per liter, and in the saturated solution in water:

$$[Ag^+] = [Cl^-] = 10^{-5}.$$

If we are dealing with the slightly soluble salt, B_2A, the expression for the solubility product becomes:

$$[B^+]^2[A^=] = S_{B_2A}. \tag{6}$$

In the saturated solution of the salt $[B^+] = 2[A^=]$, since twice as many B^+ ions are formed as $A^=$ ions:

$$B_2A \rightleftarrows 2\,B^+ + A^=.$$

It follows that:

$$1/2[B^+]^3 = 4[A^=]^3 = S_{B_2A}. \tag{7}$$

If the solubility expressed in moles per liter is again represented by s, it is seen that:

$$[A^=] = s$$

and

$$4\,s^3 = S_{B_2A}$$

$$s = \sqrt[3]{\frac{S_{B_2A}}{4}}. \tag{8}$$

Example: The solubility product of silver chromate at 25° is approximately equal to 10^{-12}. The solubility of silver chromate then is:

$$s = \sqrt[3]{\frac{10^{-12}}{4}} = 0.63 \times 10^{-4}$$

and in the saturated solution in water:

$$[CrO_4^=] = s = 0.63 \times 10^{-4}$$

and

$$[Ag^+] = 2[CrO_4^=] = 1.26 \times 10^{-4}.$$

Common-ion effect. Completeness of precipitation.

In any system in which a solid is in equilibrium with its solution, the product of the ion concentrations is determined by the solubility product. Thus, if an excess of silver ions is added to a saturated solution of silver chloride in water, the solubility product is exceeded, and consequently some silver chloride will be precipitated, equilibrium being reached when the product of the silver- and chloride-ion concentrations becomes equal to the solubility product. A similar effect will occur if an excess of chloride ions is added to a saturated silver chloride solution. In other words, a compound having an ion in common with a slightly soluble salt *decreases the solubility of the latter* (*common-ion effect*). The extent of the repression of the solubility can be easily calculated if the excess of the common ion is known. From equation (2) it follows that in any solution which is in equilibrium with the solid, BA, the following relations hold:

$$[B^+] = \frac{S_{BA}}{[A^-]} \tag{9}$$

and

$$[A^-] = \frac{S_{BA}}{[B^+]}. \tag{10}$$

If the salt has the composition BA, it is easily seen that an excess of B^+ decreases the solubility of the salt by the same amount that an equal excess of A^- does.

Example: Calculate the solubilities of silver chloride in 0.001 M, 0.01 M, and 0.1 M potassium chloride solutions respectively. $S_{AgCl} = 10^{-10}$. In 0.001 M potassium chloride $[Cl^-] = 10^{-3}$.

Therefore $$[Ag^+] = \frac{10^{-10}}{10^{-3}} = 10^{-7}.$$

In 0.01 M potassium chloride $$[Ag^+] = \frac{10^{-10}}{10^{-2}} = 10^{-8}.$$

In 0.1 M potassium chloride $$[Ag^+] = \frac{10^{-10}}{10^{-1}} = 10^{-9}.$$

In the above equations the concentration of Cl^- ions furnished by the silver chloride itself has been neglected, since it is very small compared to the concentration of the excess Cl^- ions added (see also p. 468).

Since the solubility of silver chloride in water is equal to 10^{-5}, it is found that the solubility is decreased 100 times in 0.001 M potassium chloride, 1000 times in 0.01 M potassium chloride, and 10,000 times in 0.1 M potassium chloride. In 0.001 M, 0.01 M, and 0.1 M silver nitrate solutions corresponding decreases in solubility are found (Fig. 2).

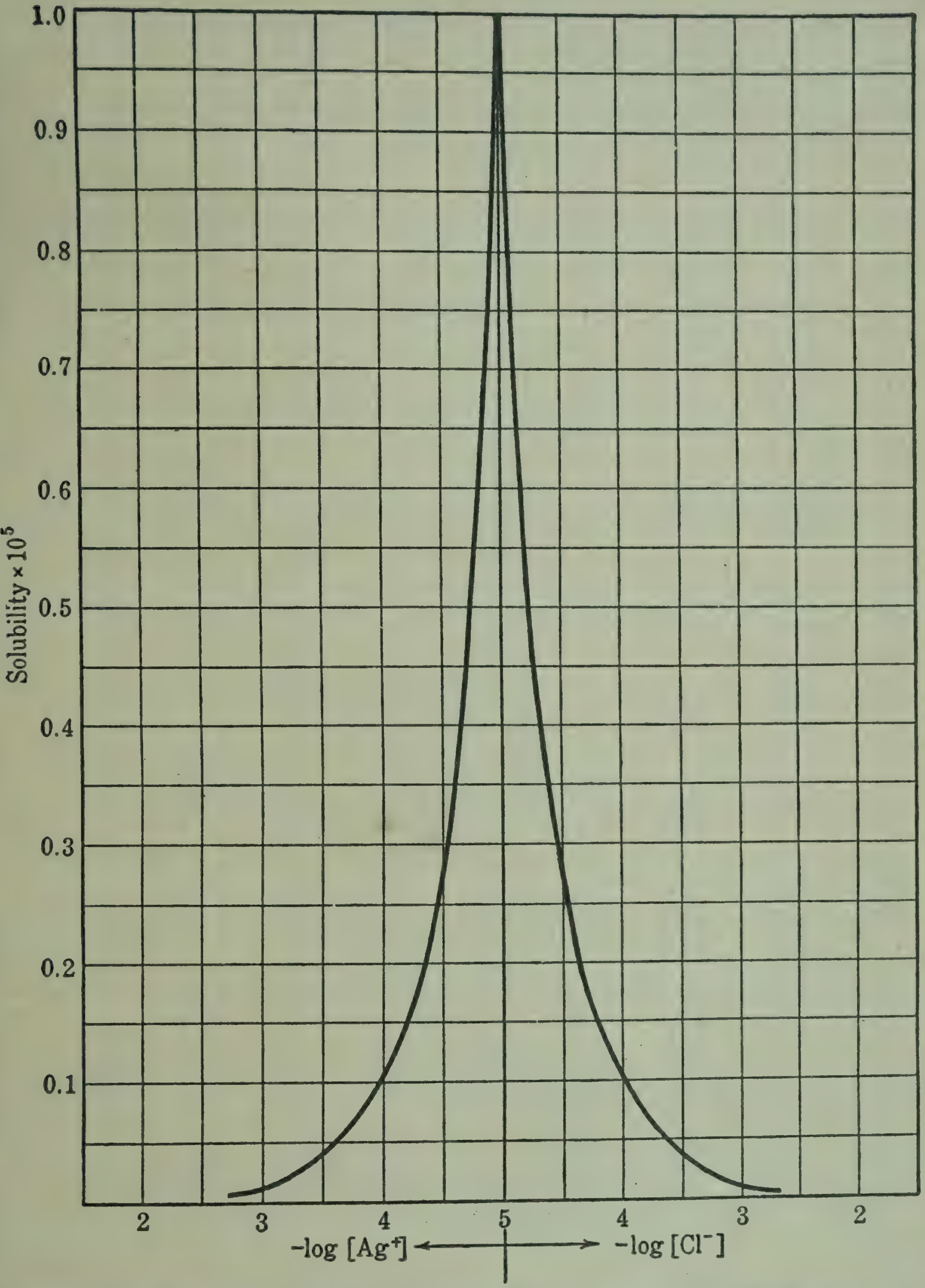


FIG. 2. Solubility of AgCl in presence of Ag^+ and Cl^- respectively.

If we are dealing with a salt of the type B_2A (see equation 6), the equilibrium conditions are expressed by:

$$[B^+] = \sqrt{\frac{S_{B_2A}}{[A^=]}} \qquad (11)$$

and

$$[A^=] = \frac{S_{B_2A}}{[B^+]^2}. \qquad (12)$$

TECHNOLOGICAL RESEARC

It is evident then that an excess of B^+ lowers the solubility to a much greater extent than the same excess of $A^=$ (cf. Fig. 3).

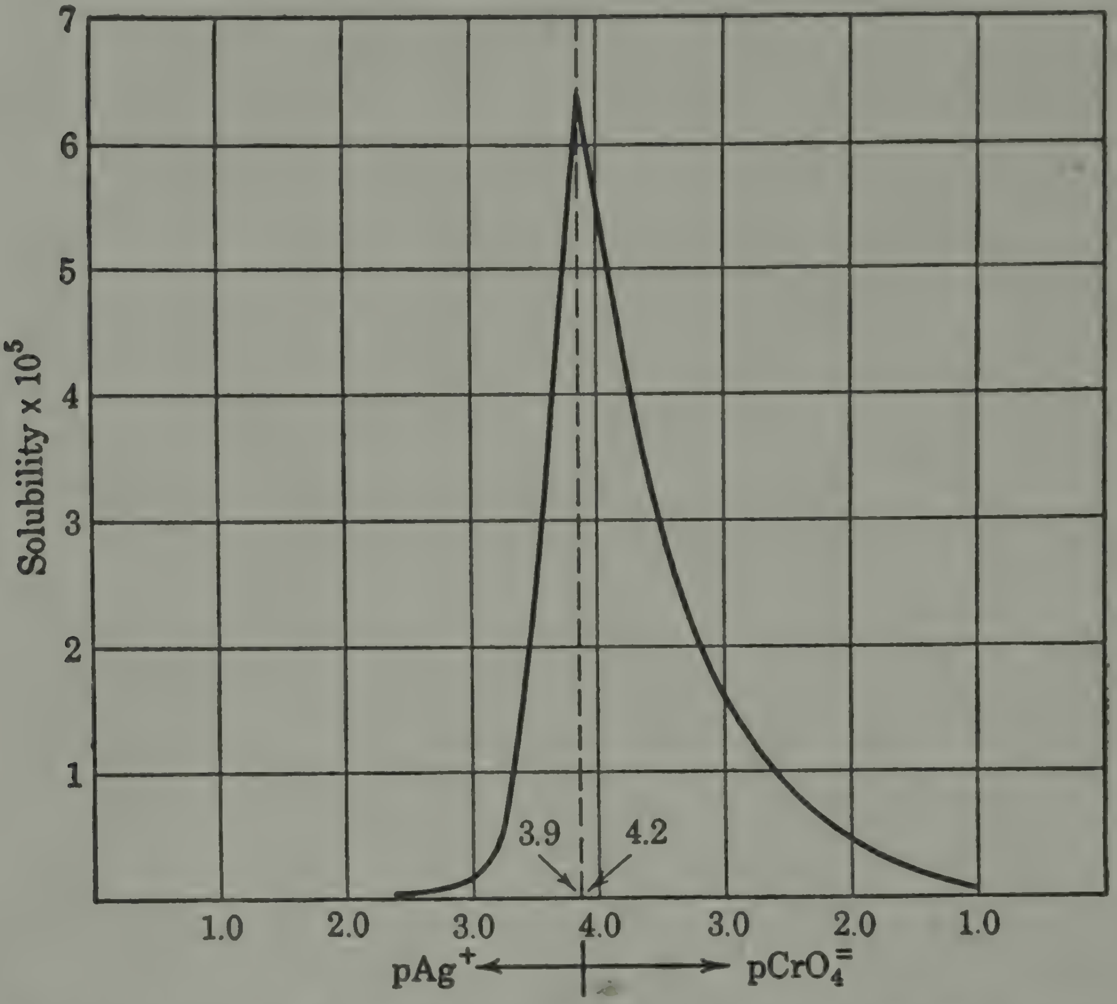


FIG. 3. Solubility of Ag_2CrO_4 in presence of Ag^+ and $CrO_4^=$ respectively.

EXAMPLE: Calculate the solubilities of silver chromate in 0.001 *M*, 0.01 *M*, 0.1 *M* silver nitrate solutions. $S_{Ag_2CrO_4} = 10^{-12}$.

In 0.001 *M* silver nitrate: $[Ag^+] = 10^{-3}$

$$[CrO_4^=] = \frac{10^{-12}}{10^{-6}} = 10^{-6}.$$

In 0.01 *M* silver nitrate: $[CrO_4^=] = 10^{-8}$.
In 0.1 *M* silver nitrate: $[CrO_4^=] = 10^{-10}$.
In 0.001, 0.01, and 0.1 *M* solutions of potassium chromate the following values of the silver concentration are found:

$$[CrO_4^=] = 0.001 \qquad [Ag^+] = \sqrt{\frac{10^{-12}}{10^{-3}}} = 3.2 \times 10^{-5}$$

$$[CrO_4^=] = 0.01 \qquad [Ag^+] = \sqrt{\frac{10^{-12}}{10^{-2}}} = 10^{-5}$$

$$[CrO_4^=] = 0.1 \qquad [Ag^+] = \sqrt{\frac{10^{-12}}{10^{-1}}} = 3.2 \times 10^{-6}$$

and the corresponding solubilities are
in K_2CrO_4: 1.6×10^{-5}, 0.5×10^{-5}, and 0.16×10^{-5}
in $AgNO_3$: 10^{-6}, 10^{-8}, and 10^{-10}.

The repression of the solubility by the common-ion effect is of great practical importance in gravimetric analysis. By adding a suitable excess of the precipitating agent, the solubility of a precipitate is usually decreased to such a small value that the loss by solubility can be neglected.

Example: How much dissolved barium sulfate is present in 200 ml. of a solution in which the barium chloride concentration is 10^{-2} molar? $S_{BaSO_4} = 10^{-10}$.

$$[SO_4^{=}] = \frac{10^{-10}}{10^{-2}} = 10^{-8}.$$

Therefore the amount of dissolved barium sulfate is:

$$\frac{200}{1000} \times 10^{-8} \times 233.4 = 4.7 \times 10^{-7} \text{ g. or } 0.00047 \text{ mg.}$$

In the table on page 54 the solubility products of some common precipitates at room temperature (about 20°) are given.

From the above one might infer that in any quantitative precipitation as large an excess of precipitating agent as possible should be added. For reasons discussed in the following paragraphs this conclusion is not correct. As a rule, the excess of reagent is limited to concentrations corresponding to 0.01 to 0.05 molar.

Solubility in solutions of electrolytes having no ion in common with the precipitate. Activity and concentration.

Thus far in our applications of the mass-action law we have assumed that *concentrations* can be written instead of *active masses* (see the statement of the mass-action law, p. 32). This is only approximately true but is usually permissible in our general discussions. Therefore, the approximation is made throughout this text. In some cases, however, it is necessary to use a more exact expression in order to interpret certain effects. The exact formulation of the salt effect demands a knowledge of thermodynamics. Therefore the present discussion will be limited to an incomplete and elementary outline.

The active mass of a substance in solution is given by its *activity* and not by its *concentration.* The following relation exists between the concentration c and the activity a:

$$a = cf \tag{13}$$

in which f represents the *activity coefficient* of the particular component. The activity coefficient of an ion is strongly affected by the presence of other ions in the solution. In infinitely dilute solutions f approaches unity, and then a becomes equal to c. With increasing ionic concentration f decreases until finally a minimum value is reached. The activity coefficient of an ion in an electrolyte solution depends upon its valence, its individual properties, and upon the concentration and kind of the other ions present. In the application of the mass-action law activities should be written instead of concentrations. In dealing with the slightly soluble salt, BA, the exact expression becomes:

$$a_{B^+} \cdot a_{A^-} = S_{BA} \tag{14}$$

TABLE II. SOLUBILITY PRODUCTS S OF SOME SLIGHTLY SOLUBLE SALTS[1] AT ROOM TEMPERATURE

(pS denotes negative logarithm of $S = -\log S$.)

SALT		S	$pS = -\log S$
Ag salts:	Bromate	5.0×10^{-5}	4.3
	Bromide	4.0×10^{-13}	12.6
	Carbonate	5.0×10^{-12}	11.3
	Chloride	1.1×10^{-10}	9.96
	Chromate	2.0×10^{-12}	11.7
	Cyanide	4.0×10^{-12}	11.4
	Hydroxide	2.0×10^{-8}	7.7
	Iodate	2.0×10^{-8}	7.7
	Iodide	1.0×10^{-16}	16.0
	Oxalate	5.0×10^{-12}	11.3
	Thiocyanate	1.0×10^{-12}	12.0
Ba salts:	Carbonate	7.0×10^{-9}	8.16
	Chromate	2.0×10^{-10}	9.7
	Iodate	6.0×10^{-10}	9.22
	Oxalate	1.7×10^{-7}	6.77
	Sulfate	1.0×10^{-10}	10.0
Ca salts:	Carbonate	1.2×10^{-8}	7.92
	Fluoride	3.5×10^{-11}	10.46
	Oxalate	2.0×10^{-9}	8.7
	Sulfate	6.1×10^{-5}	4.22
Cuprous salts:	Iodide	5.0×10^{-12}	11.3
	Thiocyanate	1.6×10^{-11} (?)	10.8 (?)
Mercurous salts:	Bromide (Hg_2Br_2)	$3 \quad \times 10^{-23}$	22.5
	Chloride (Hg_2Cl_2)	$6 \quad \times 10^{-19}$	18.2
Mg salts:	Carbonate	2.0×10^{-4}	3.7
	Fluoride	7.0×10^{-9}	8.16
	Hydroxide	1.2×10^{-11}	10.92
	$MgNH_4PO_4 \cdot 6\,H_2O$	2.5×10^{-13}	12.6
	Oxalate	8.6×10^{-5}	4.07
Pb salts:	Carbonate	3.3×10^{-14}	13.48
	Chromate	1.8×10^{-14}	13.75
	Fluoride	7.0×10^{-9}	8.15
	Iodate	$3 \quad \times 10^{-13}$	12.5
	Oxalate	3.4×10^{-11}	10.47
	Sulfate	1.0×10^{-8}	8.0
Sr salts:	Carbonate	1.6×10^{-9}	8.80
	Oxalate	5.0×10^{-8}	7.3
	Sulfate	2.8×10^{-7}	6.56
Thallous salts:	Bromide	2.0×10^{-6}	5.7
	Chloride	1.5×10^{-4}	3.82
	Iodate	2.2×10^{-6}	5.66
	Iodide	2.8×10^{-8}	7.55

---

[1] For solubility products of metal sulfides see Table XIII, p. 64.

in which a_{B^+} denotes the activity of the B ions and a_{A^-} that of the A ions. Combination of (13) and (14) yields:

$$[B^+][A^-]f_B f_A = S_{BA} \tag{15}$$

in which f_B and f_A denote the activity coefficients of B^+ and A^- respectively. In dealing with a saturated solution of a slightly soluble salt, BA, in water the ion concentrations are so small that f_B and f_A become virtually equal to 1. On addition of an electrolyte having no ion in common with BA, f_B and f_A decrease.

$$[B^+][A^-] = \frac{S_{BA}}{f_B f_A}. \tag{16}$$

Since S_{BA} is a true constant, a decrease in the value of the product $f_B f_A$ results in an increase of the product $[B^+][A^-]$. *This means that the solubility of a slightly soluble salt generally increases in a solution of an electrolyte which has no ion in common with the precipitate.* This effect may be called the *salt effect.* It depends upon the valence of the ions of the precipitate and the kind of electrolyte. It increases strongly with increasing valence of the ions of the precipitate. Two examples are given in Table III and Figure 4.

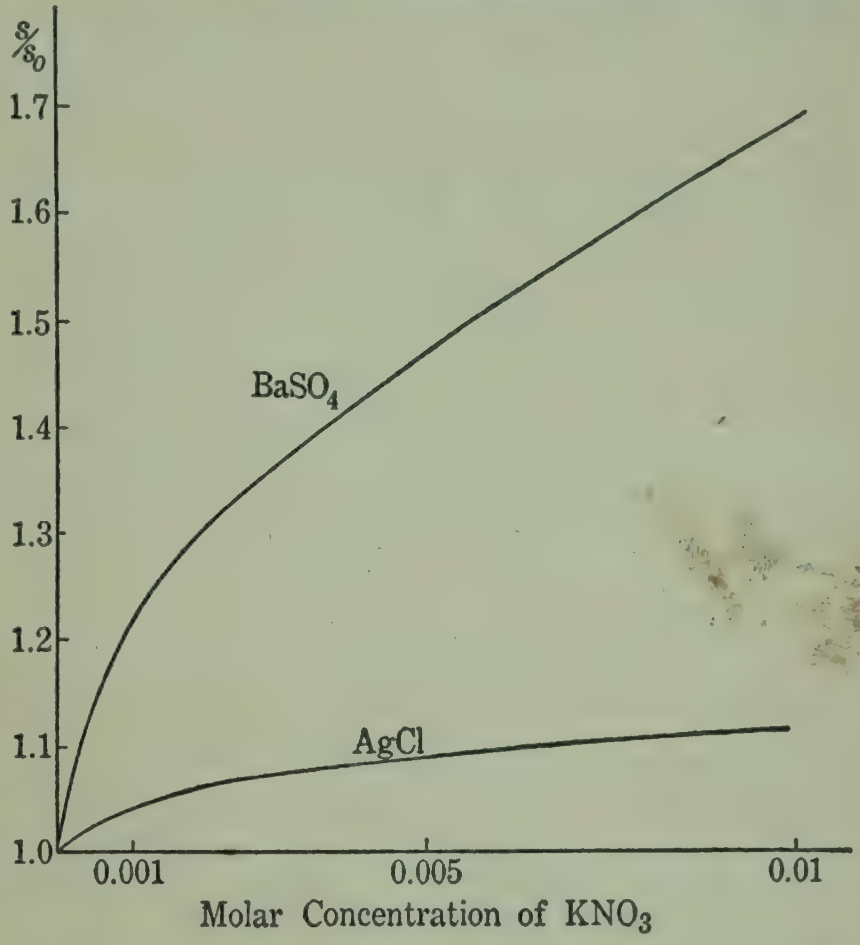


FIG. 4. Relative increase in solubility of silver chloride and barium sulfate in potassium nitrate solution.

TABLE III. SOLUBILITY OF SILVER CHLORIDE [1] AND BARIUM SULFATE [2] IN DILUTE POTASSIUM NITRATE SOLUTIONS AT 25°

(s_o = solubility in water; s = solubility in electrolyte solution)

CONCENTRATION OF KNO_3 MOLARITY	AgCl $s \times 10^5$	s/s_0	CONCENTRATION OF KNO_3 MOLARITY	$BaSO_4$ $s \times 10^5$	s/s_0
0	1.278 (s_o)	1.00	0	0.96 (s_o)	1.00
0.001	1.325	1.04	0.001	1.16	1.21
0.005	1.385	1.08	0.005	1.42	1.48
0.01	1.427	1.12	0.01	1.63	1.70
			0.036	2.35	2.45

---

[1] S. Popoff and E. W. Neuman, J. Phys. Chem. *34*, 1853 (1930).

[2] E. W. Neuman, J. Am. Chem. Soc. *55*, 879 (1933).

TABLE IV. SOLUBILITY OF CALCIUM OXALATE MONOHYDRATE IN SODIUM CHLORIDE SOLUTIONS AT 37°[1]

CONCENTRATION NaCl, MOLARITY	0	0.005	0.01	0.04	0.1	0.4	0.6
Solubility $CaC_2O_4 \cdot H_2O$, molarity $\times 10^{-3}$	0.055	0.082	0.091	0.12	0.16	0.26	0.2

The relative increase in the solubility of silver chloride in a given electrolyte solution is much less than that of barium sulfate or calcium oxalate in the same solution, because in the former case the salt consists of two univalent ions and in the latter case of two divalent ions (see Fig. 4).

It is evident that the common-ion effect is counteracted by the salt effect. Increasing the concentration of the common ion in the solution results in a decrease in the solubility, which is partly compensated by the salt effect. This is one of the reasons why a very large excess of the precipitating ion is avoided in quantitative precipitations (see also the paragraph on complex formation).

As an illustration we give in Table V some data on the solubility of lead sulfate in sodium sulfate solutions at 25°.[2]

TABLE V. SOLUBILITY OF LEAD SULFATE IN SODIUM SULFATE SOLUTIONS

Molarity, Na_2SO_4	0	0.001	0.01	0.02	0.04	0.100	0.200	0.500
Solubility $PbSO_4$ in moles $\times 10^5$ per liter	15.2	2.4	1.6	1.4	1.3	1.6	2.3	2.3
Solubility calculated from solubility product	15.2	2.3	0.23	0.11	0.055	0.02	0.0064	0.0048

The values in the bottom row are calculated from the solubility product, concentrations being used instead of activities. It is seen that only in the very dilute 0.001 *M* sulfate solution is the calculated value about equal to the experimental value. In 0.01 *M* sulfate solution the experimental solubility is already seven times greater than the calculated one. The difference between the two increases with increasing sulfate concentration. Actually a minimum solubility is found in about 0.05 *M* sulfate. From the above, it is evident that in any exact calculation activities instead of concentrations should be used.

Influence of temperature upon solubility.

When heat is absorbed in the solution of a salt, the solid phase of which is in equilibrium with the solution,

$$BA + \text{heat} \rightleftarrows B^+ + A^-$$

---

[1] G. Hammarsten, Compt. rend. Lab. Carlsberg *17*, No. 11 (1929).

[2] I. M. Kolthoff, R. W. Perlich, and D Weiblen, J. Phys. Chem. *46*, 561 (1942).

raising the temperature of the solution will increase the solubility of the salt according to the theorem of Le Chatelier-van't Hoff (see p. 33). Most of the precipitates dealt with in quantitative analysis are more soluble in hot than in cold solution. In the case of silver chloride the temperature effect is very pronounced (see Table VI); in the case of barium sulfate it is less so, but still distinct (Table VII).

TABLE VI. SOLUBILITY OF SILVER CHLORIDE AT DIFFERENT TEMPERATURES

TEMP. ° C.	10	25	50	100
Solubility, mg. per liter	0.89	1.72	5.23	21.1

TABLE VII. SOLUBILITY OF BARIUM SULFATE AT DIFFERENT TEMPERATURES

TEMP. ° C.	0	10	25	50	100
Solubility, mg. per liter	1.9	2.2	2.8	3.36	3.9

The presence of an excess of the precipitating agent usually diminishes the solubility to such an extent that the temperature effect becomes negligibly small. However, the double phosphates of ammonium with magnesium, manganese, or zinc, as well as lead sulfate and strontium sulfate, are usually filtered at room temperature to avoid appreciable solubility losses.

Influence of the solvent.

As a rule, the solubility of inorganic compounds in water is decreased by the addition of organic solvents, such as methyl, ethyl, and propyl alcohols, acetone, etc. For example, the solubility of calcium sulfate in 50 per cent ethyl alcohol is so small that a quantitative precipitation of calcium can be effected in this medium. In general, care must be taken not to add too much of an organic solvent or else salts other than the desired one may be precipitated also. Sometimes an organic solvent is used instead of water to separate certain constituents of a mixture.

Lithium chloride, for example, is soluble in amyl alcohol, whereas sodium and potassium chlorides are practically insoluble, and lithium may thus be separated from the other alkalies. Use is made of organic solvents in the determination of potassium as potassium perchlorate (p. 414). The solubility of the latter in organic solvents is much smaller than in water, as shown by the solubility data of Willard and Smith,[1] whereas sodium perchlorate is quite soluble in such solvents. In the separation of potassium from sodium by this method, sulfate should be absent, as sodium sulfate is completely insoluble in organic solvents.

---

[1] H. H. Willard and G. F. Smith, J. Am. Chem. Soc. *45*, 286 (1923).

TABLE VIII. SOLUBILITY OF POTASSIUM PERCHLORATE IN ORGANIC SOLVENTS AT 25° [1]

SOLVENT	WATER	METHANOL	ETHANOL	*n*-PROPANOL	*n*-BUTANOL	ETHYL ACETATE	ACETONE
Solubility, in g. per 100 g. sat. sol.	2.02	0.105	0.012	0.010	0.0045	0.0015	0.155

In general, the effect of the organic solvent upon the solubility increases with increasing valence of the cation and the anion of the slightly soluble salt. Thus, the effect of the addition of ethanol upon the solubility is much greater in the case of salts like barium, calcium, and lead sulfate than in the case of a salt like potassium perchlorate. The decrease in the solubility of lead sulfate with increasing ethanol concentration in water-ethanol mixtures [2] is shown in Table IX.

TABLE IX. SOLUBILITY OF LEAD SULFATE IN WATER-ETHANOL MIXTURES

CONCENTRATION ETHANOL IN VOLUME PER CENT	0	10	20	30	40	50	60	70
Solubility of $PbSO_4$ in mg. per liter	30	11	4.2	1.5	0.51	0.32	0.20	0.06
Solubility of $PbSO_4$ in moles per liter $\times 10^{-5}$	15	5.4	2.1	0.76	0.25	0.16	0.10	0.03

Influence of formation of complex ions.

In the discussion of the common-ion effect it was mentioned that in quantitative precipitations a large excess of precipitating agent should usually be avoided. Many precipitates show a tendency to form complex ions with an excess of their own ions, resulting in an increase in the solubility. A most striking example is found in the behavior of silver cyanide with an excess of alkali cyanide. If cyanide is added to a silver nitrate solution, silver cyanide is precipitated. (Actually the composition of the precipitate is not AgCN but $Ag[Ag(CN)_2]$.) After the addition of an amount of cyanide equivalent to the silver present, a quantitative precipitation of the silver will have been effected, since the solubility product of silver cyanide is equal to 4×10^{-12}. Therefore, at this point

---

[1] H. H. Willard and G. F. Smith, J. Am. Chem. Soc. *45*, 286 (1923).

[2] I. M. Kolthoff, R. W. Perlich, and D. Weiblen, J. Phys. Chem. *46*, 561 (1942).

$[Ag^+] = [CN^-] = \sqrt{4 \times 10^{-12}} = 2 \times 10^{-6}$. On the addition of an excess of cyanide the silver cyanide begins to dissolve because of the formation of the complex ion $Ag(CN)_2^-$:

$$AgCN + CN^- \rightleftarrows Ag(CN)_2^-.$$

Application of the mass-action law yields:

$$\frac{[AgCN][CN^-]}{[Ag(CN)_2^-]} = K.$$

As long as silver cyanide remains present as a solid phase, [AgCN] will be constant. Therefore in this particular case it is found that

$$\frac{[CN^-]}{[Ag(CN)_2^-]} = K' = 10^{-10}. \tag{17}$$

Suppose now that the excess of cyanide added to the solution corresponds to a concentration of 0.01 molar. Part of the cyanide remains unchanged, and another part is transformed into the complex silver cyanide ion:

$$AgCN + CN^- \rightleftarrows Ag(CN)_2^-.$$

Therefore $$[CN^-] + [Ag(CN)_2^-] = 10^{-2}. \tag{18}$$

From (17) and (18) it is found that when equilibrium is attained,

$$[CN^-] = 10^{-12} \text{ and } [Ag(CN)_2^-] = 10^{-2} - 10^{-12} = 10^{-2}.$$

It is evident then that practically all of the cyanide added is quantitatively transformed into complex silver cyanide ion and that potassium cyanide dissolves an equivalent amount of silver cyanide.

Other slightly soluble metal cyanides show a behavior similar to that of silver cyanide, although the complexes formed are less stable than the silver cyanide complex.

Another example of the solution of a precipitate in an excess of precipitating agent is found with mercuric iodide. The red precipitate dissolves readily in an excess of iodide:

$$HgI_2 + 2\,I^- \rightleftarrows HgI_4^=.$$

With most of the ordinary precipitates the complexes formed with an excess of the common ion are much less stable than those mentioned above. As a rule, it is found that the solubility first decreases with an excess of the precipitating ion as is to be expected from the common-ion effect. The repression of the solubility, however, may be counteracted by the tendency to form complexes. Therefore, a minimum solubility may be found at a certain excess of common ion, and the solubility then increases with the increasing concentration of the latter. This is clearly shown in the following tables, in which the solubility of silver chloride in sodium chloride solutions of various concentrations is given. A minimum solubility is found in approximately 0.004 N sodium chloride solution. The very slightly soluble silver iodide shows a pronounced tendency to form complexes with an excess of iodide or silver ions. Although its solubility in water is equal to 10^{-8}, it increases to 2×10^{-3} in 0.5 N KI, to 1.48×10^{-2} in 1 N KI, to 2.9×10^{-4} in 0.2 N $AgNO_3$, to 1.27×10^{-3} in 0.5 N $AgNO_3$, and to 1.3×10^{-2} in 1.2 N $AgNO_3$ solution.

TABLE X. SOLUBILITY OF SILVER CHLORIDE IN DILUTE SODIUM CHLORIDE SOLUTIONS [1]

CONCENTRATION NaCl, EQUIV. PER LITER	(0)	0.0039	0.0092	0.036	0.088	0.35	0.5
Solubility AgCl, equiv. per liter $\times 10^3$	(0.013)	0.00072	0.00091	0.0019	0.0036	0.017	0.028

TABLE XI. SOLUBILITY OF SILVER CHLORIDE IN CONCENTRATED SODIUM CHLORIDE SOLUTIONS [2]

CONCENTRATION NaCl, EQUIV. PER LITER	(0)	0.9	1.4	1.93	2.87	3.82
Solubility AgCl, equiv. per liter $\times 10^3$	(0.013)	0.10	0.18	0.39	10.00	24.91

Complex ions may also be formed with constituents other than the common ion present in the solution. It is well known, for example, that many of the slightly soluble metal hydroxides dissolve in ammonia with the formation of complex ammonio ions.

$$AgOH + 2\,NH_3 \rightleftarrows Ag(NH_3)_2^+ + OH^-.$$

The increase in solubility in this case is determined by the complex formation between silver ions and ammonia, which may be represented by the following reversible reaction:

$$Ag^+ + 2\,NH_3 \rightleftarrows Ag(NH_3)_2^+$$

$$\frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]} = K = 7 \times 10^{-8}. \qquad (19)$$

The constant K is called the complex dissociation constant or the instability constant of the complex; its reciprocal value gives the stability constant of the complex.

---

[1] G. S. Forbes and H. I. Cole, J. Am. Chem. Soc. *43*, 2492 (1921).
[2] J. Kendall and C. H. Sloan, J. Am. Chem. Soc. *47*, 2306 (1925).

As a result of the complex formation, ammonium hydroxide will increase the solubility of any slightly soluble silver compound. Let us calculate, for example, the solubility of silver bromide in 1 *N* ammonium hydroxide and assume that after equilibrium is reached $[NH_3] = 1$.

$$[Ag^+][Br^-] = 4 \times 10^{-13}. \tag{20}$$

It is seen that in a saturated solution of silver bromide in ammonium hydroxide the total amount of dissolved silver in equivalents is equal to the amount of dissolved bromide in equivalents.

$$[Ag^+] + [Ag(NH_3)_2^+] = [Br^-] = \text{solubility of AgBr}. \tag{21}$$

From (19) it is found that

$$\frac{[Ag^+]}{[Ag(NH_3)_2^+]} = 7 \times 10^{-8} \tag{22}$$

since NH_3 is equal to 1. Then

$$[Ag(NH_3)_2^+] = \frac{[Ag^+]}{7 \times 10^{-8}}. \tag{23}$$

Equations (21) and (23) give

$$[Ag^+] + \frac{[Ag^+]}{7 \times 10^{-8}} = [Br^-]. \tag{24}$$

Equations (20) and (24) yield the relation

$$[Ag^+]\left\{[Ag^+] + \frac{[Ag^+]}{7 \times 10^{-8}}\right\} = 4 \times 10^{-13}$$

$$[Ag^+] = 1.7 \times 10^{-10}$$

$$\text{and} \quad [Ag(NH_3)_2^+] = \frac{[Ag^+]}{7 \times 10^{-8}} = \frac{1.7 \times 10^{-10}}{7 \times 10^{-8}} = 2.4 \times 10^{-3} \qquad \text{(eq. 23)}$$

$$[Br^-] = [Ag^+] + [Ag(NH_3)_2^+] = 2.4 \times 10^{-3}. \qquad \text{(eq. 21)}$$

Whereas the solubility of silver bromide in water is equal to 6.3×10^{-6} mole per liter, it is increased to 2.6×10^{-3} mole per liter in 1 *N* ammonium hydroxide.

In chemical separations use is often made of the fact that one constituent can be transformed into a complex which is no longer precipitable with the precipitating agent, whereas another constituent is precipitated. Examples are given in the chapter on "Separations" (see p. 72).

Influence of the hydrogen-ion concentration.

If we are dealing with a slightly soluble salt of a strong acid, such as a silver halide, acids will have the same effect upon its solubility as any other indifferent electrolyte (see the paragraph on the solubility in electrolytes having no ion in common with the precipitate, p. 53). If the slightly soluble salt is the salt of a weak acid, then strong acids will have a solvent effect upon it. Consider a salt such as calcium fluoride:

$$CaF_2 \rightleftarrows Ca^{++} + 2\,F^-. \tag{25}$$

If a strong acid is added to a suspension of this salt, hydrogen ions will combine with fluoride ions since hydrofluoric acid is a relatively weak acid:

$$F^- + H^+ \rightleftarrows HF. \tag{26}$$

Therefore the equilibrium in equation (25) is displaced to the right since fluoride ions disappear. Equilibrium is again attained when $[Ca^{++}][F^-]^2$ has become equal to the solubility product of calcium fluoride.

It is a relatively simple matter to derive a relation between the solubility at a certain hydrogen-ion concentration, the solubility product of the salt, and the ionization constant. It is evident that the solvent effect of acids increases with an increase in the solubility product of the salt and a decrease in the ionization constant of the weak acid. In quantitative precipitations the solvent effect of acids must often be taken into consideration. All carbonates, for example, dissolve in acids; most of the slightly soluble phosphates, arsenates, chromates, fluorides, sulfites, cyanides (with the exception of silver cyanide, which actually is a salt of the strong acid, $H[Ag(CN)_2]$), oxalates, and salts of other organic acids dissolve in strong acids. Sometimes a quantitative precipitation can be obtained in weakly acid medium (pH = 4) as is the case in the precipitation of calcium oxalate and various fluorides. On the other hand, magnesium ammonium phosphate and most other phosphates are so soluble at this pH that they must be precipitated from a weakly alkaline medium.

The solvent effect of acids is of importance even in the case of slightly soluble sulfates. Although sulfuric acid is usually considered to be a strong electrolyte, its second dissociation is not complete, and solutions of sulfuric acid have a lower hydrogen-ion concentration than those of hydrochloric, perchloric, or nitric acids of the same equivalent concentration:

$$\begin{aligned} H_2SO_4 &\rightleftarrows H^+ + HSO_4^- \quad \textit{(complete)}\\ HSO_4^- &\rightleftarrows H^+ + SO_4^= \quad \textit{(incomplete)}\\ \frac{[H^+][SO_4^=]}{[HSO_4^-]} &= 3 \times 10^{-2}. \end{aligned}$$

Since the sulfate ions have a tendency to combine with hydrogen ions, the solubility of sulfates will increase in acid solutions. Barium, lead, and strontium sulfates are all more soluble in solutions of strong acids than in water. The effect of nitric acid is shown in Table XII.

TABLE XII. SOLUBILITY OF BARIUM SULFATE IN NITRIC ACID [1]

CONCENTRATION HNO_3, MOLARITY	0.05	0.1	0.5	1.0	2.0
Molar solubility $BaSO_4 \times 10^3$ at 19°	0.9	1.2	3.9	7.7	11.9
Molar solubility $BaSO_4 \times 10^3$ at 100°	7.7		26.5	41.6	

In spite of the fact that barium sulfate has a higher solubility in acid than in neutral medium, it is usually precipitated from dilute acid solutions in order to obtain a precipitate which is more easily filterable. In this particular case the effect of an excess of the common ion compensates the solvent effect of the medium.

The influence of the acidity upon the solubility of slightly soluble metal sulfides is of special analytical importance. Hydrogen sulfide is a very weak acid which dissociates in two steps:

$$H_2S \rightleftarrows H^+ + HS^- \tag{27}$$

$$HS^- \rightleftarrows H^+ + S^= \tag{28}$$

$$\frac{[H^+][HS^-]}{[H_2S]} = K_1 = 8.4 \times 10^{-8} \tag{29}$$

$$\frac{[H^+][S^=]}{[HS^-]} = K_2 = 1.2 \times 10^{-15}. \tag{30}$$

A saturated solution of a divalent metal sulfide in water does not contain equal amounts of metal and sulfide ions but an excess of metal ions since most of the sulfide ions are hydrolyzed to HS^- and H_2S:

$$MS \rightarrow M^{++} + S^=$$

$$S^= + H_2O \rightleftarrows HS^- + OH^-$$

$$(S^= + 2\,H_2O \rightleftarrows H_2S + 2\,OH^-).$$

In the precipitation of metal ions with hydrogen sulfide in acid medium the sulfide-ion concentration is extremely small. Still, under equilibrium conditions it is found that the following relation holds in the suspension of any metal sulfide:

$$[M^{++}][S^=] = S_{MS}. \tag{31}$$

Multiplication of equation (29) by (30) yields

$$\frac{[H^+]^2[S^=]}{[H_2S]} = K_1K_2 = 10^{-22}. \tag{32}$$

From (31) and (32) the amount of metal sulfide dissolved, which is equal to $[M^{++}]$, is found to be

$$[M^{++}] = \frac{S_{MS}}{[S^=]} = \frac{S_{MS}[H^+]^2}{10^{-22}[H_2S]}. \tag{33}$$

---

[1] I. M. Kolthoff and E. H. Vogelenzang, Z. anal. Chem. *58*, 49 (1919).

Therefore the solubility of the sulfide increases with the square of the hydrogen-ion concentration. If the solution is saturated with hydrogen sulfide at room temperature, $[H_2S]$ = constant = *ca.* 0.1. Therefore, if the solubility product is known, the solubility of the sulfide in solutions saturated with hydrogen sulfide can be calculated for any hydrogen-ion concenrtation.

If the metal is univalent (Ag^+, Tl^+), a slightly different expression is obtained:

$$[M^+] = \sqrt{\frac{S_{MS}[H^+]^2}{10^{-22}[H_2S]}}. \tag{34}$$

The solubility products, S_{MS}, of the various metal sulfides are given in Table XIII; pS_{MS} denotes the negative logarithm of the solubility product. In the column headed *M* the solubility of the sulfide is given (which is equal to the metal-ion concentration in a solution 1 *N* with respect to hydrogen ions and saturated with hydrogen sulfide, provided that there is equilibrium between the solid and the solution). In the application of these figures to the precipitation of metal sulfides from dilute acid solutions, it should be understood that the speed of precipitation of many of them is very slow. A solution of 0.1 *M* zinc sulfate in 1 *N* hydrochloric acid, for example, remains clear when saturated with hydrogen sulfide. Still, the solution is supersaturated with respect to zinc sulfide, since the equilibrium concentration corresponds to about 0.006 *M* zinc. The zinc sulfide will finally precipitate if the solution is kept saturated with hydrogen sulfide for a month or so. Precipitation once started is catalyzed by the solid sulfide formed (compare "postprecipitation," p. 113).

TABLE XIII. SOLUBILITY PRODUCTS (S_{MS}) OF SULFIDES AND THEIR NEGATIVE LOGARITHMS, pS_{MS}

$[M]$ denotes the solubility in a solution saturated with H_2S at $[H^+] = 1$

METAL SULFIDE	S_{MS}	pS_{MS}	$[M]$
MnS (flesh-colored)	7.0×10^{-16}	15.16	6.3×10^{7}
MnS (green)	6.2×10^{-22}	21.21	5.6×10^{1}
FeS	$3.3 \times 10^{-19} - 1 \times 10^{-18}$	18.5 – 18	3×10^{4}[a] $- 9 \times 10^{4}$[b]
Tl_2S	1.2×10^{-24}	23.92	3.3×10^{-1}
ZnS	7×10^{-26}	25.2	6.3×10^{-3}
CoS	1.9×10^{-27}	26.72	1.7×10^{-4}
NiS	1.1×10^{-27}	26.96	1.0×10^{-5}
CdS (from $CdCl_2$)	7.1×10^{-28}	27.15	6.5×10^{-5}
CdS (from $CdSO_4$)	5.1×10^{-29}	28.29	4.6×10^{-6}
PbS	3.4×10^{-28}	27.47	3.1×10^{-5}
Bi_2S_3	1.6×10^{-72} (?)	71.8	3.5×10^{-2}
CuS	3.5×10^{-42}	41.46	3×10^{-19}
Ag_2S	1×10^{-50}	50	3×10^{-14}
Hg_2S	1×10^{-47}	47	1×10^{-12}
HgS	3×10^{-54}	53.5	3×10^{-31}

[a] aged; [b] fresh; see I. M. Kolthoff and F. S. Griffith, J. Am. Chem. Soc. *60*, 2036 (1938).

Fractional precipitation.

If two anions form slightly soluble salts with the same cation or if two cations form slightly soluble compounds with the same anion, the less soluble compound will precipitate first on the addition of a precipitating agent to a solution containing both. It is a matter of practical importance to investigate how completely the one ion can be precipitated before the second ion reacts with the reagent.

Let us consider the case in which we have a mixture of iodide and chloride which is treated with silver nitrate. Silver iodide being less soluble than silver chloride precipitates first, and after most of the iodide has reacted the chloride will precipitate. When the silver chloride begins to separate, the supernatant liquid is in equilibrium with the two solid phases, AgI and AgCl. This means that the following relations are satisfied:

$$[\mathrm{Ag}^+][\mathrm{I}^-] = S_{\mathrm{AgI}} = 10^{-16} \qquad (35)$$

$$[\mathrm{Ag}^+][\mathrm{Cl}^-] = S_{\mathrm{AgCl}} = 10^{-10}. \qquad (36)$$

From (35) and (36) it is found that

$$[\mathrm{Ag}^+] = \frac{S_{\mathrm{AgI}}}{[\mathrm{I}^-]} = \frac{S_{\mathrm{AgCl}}}{[\mathrm{Cl}^-]} \qquad (37)$$

or, when both AgI and AgCl are present as solid phases,

$$\frac{[\mathrm{Cl}^-]}{[\mathrm{I}^-]} = \frac{S_{\mathrm{AgCl}}}{S_{\mathrm{AgI}}} = \frac{10^{-10}}{10^{-16}} = 10^6. \qquad (38)$$

When $\frac{[\mathrm{Cl}^-]}{[\mathrm{I}^-]}$ is smaller than 10^6, the solubility product of silver chloride is not exceeded, and on addition of silver nitrate to the mixture silver iodide will precipitate until the above ratio has become 10^6. From then on, further addition of silver nitrate will result in a precipitation of the chloride.

If we start with a solution which is 0.01 N in potassium iodide and 0.1 N in potassium chloride, silver iodide alone will be precipitated on addition of silver nitrate until the iodide concentration has become equal to $\frac{[\mathrm{Cl}^-]}{10^6} = 10^{-7}$, or only 0.001 per cent of the original iodide remains in the solution. The separation of iodide and chloride is quantitative and could be applied for quantitative purposes if the point at which the iodide precipitation is complete could be indicated in some way or other. In volumetric analysis this can be done by using iodine-starch as an indicator. This remains blue until all of the iodide has reacted and then changes with more silver nitrate to colorless before silver chloride precipitates. In the use of a silver electrode in potentiometric titrations an abrupt change of the potential of the electrode indicates the completeness of the precipitation of the iodide. In the chapter on "Separations" (p. 68) and in the discussion of precipitation methods in Volumetric Analysis (Mohr's method, p. 471), we shall meet with other cases where use is made of fractional precipitation.

PROBLEMS

1. The solubility product of silver chloride at room temperature is equal to 1.1×10^{-10}. What is the solubility of the salt in (a) water, (b) 0.01 *M* sodium chloride, (c) 0.01 *M* silver nitrate?

Ans. (a) 1.05×10^{-5} *M*; (b) 1.1×10^{-8} *M*; (c) 1.1×10^{-8} *M*.

2. At 100° the solubility of silver chloride in water is equal to 21.1 mg. per liter. Calculate (a) the solubility product at 100°, (b) the molar solubility in water at 100°, (c) the molar solubility in 0.01 *M* sodium chloride.

Ans. (a) 2.16×10^{-8}; (b) 1.47×10^{-4}; (c) 2.16×10^{-6}.

3. The solubility product of magnesium hydroxide is 1.2×10^{-11}. The base is completely dissociated in its saturated solution. Calculate (a) the solubility of the hydroxide in water, (b) the hydroxyl-ion concentration in the saturated solution in water, (c) the magnesium-ion concentration in the solution, (d) the magnesium-ion concentration in a saturated solution in 0.01 *N* sodium hydroxide, (e) the solubility in 0.01 *M* magnesium chloride.

Ans. (a) 1.44×10^{-4} *M*; (b) 2.88×10^{-4}; (c) 1.44×10^{-4}; (d) 1.2×10^{-7}; (e) 1.73×10^{-5} *M*.

4. A solution of magnesium chloride is added with stirring to a mixture 0.5 *N* with respect to ammonia and 0.9 *N* with respect to ammonium chloride. What is the magnesium-ion concentration in the solution at the moment when a permanent precipitate of magnesium hydroxide is formed? The ionization constant of ammonia is 1.8×10^{-5}. *Ans.* $[Mg^{++}] = 0.12$.

5. The solubility of silver iodate in 0.5 *M* potassium nitrate is 2.67×10^{-4} *M* at 25°. To 500 ml. of the saturated solution is added 0.0005 mole of solid silver nitrate. Calculate the final silver and iodate concentrations in the solution, the amount of silver iodate precipitated, and the amount of silver iodate left in solution.

Ans. $[Ag^+] = 1.068 \times 10^{-3}$; $[IO_3^-] = 6.8 \times 10^{-5}$; $AgIO_3$ precipitated $= 0.0282$ g.; $AgIO_3$ left in solution $= 0.0096$ g.

6. Calculate the solubility of calcium oxalate in a buffer solution with a pH of 4. The solubility product of calcium oxalate is 2.0×10^{-9}. The second ionization constant of oxalic acid

$$\frac{[H^+][C_2O_4^=]}{[HC_2O_4^-]} = 6 \times 10^{-5}$$

In solving this problem, realize that

$$[Ca^{++}] = [C_2O_4^=] + [HC_2O_4^-].$$

Ans. 7.3×10^{-5} *M*.

7. The solubility product of silver iodate in pure water is 3×10^{-8} and that of silver chloride 10^{-10} at room temperature. 100 ml. of 0.1 *M* silver nitrate are added to 100 ml. of a mixture 0.1 *M* in chloride and 0.1 *M* in iodate. (a) What is the sum of the concentrations of chloride and iodate after the addition of silver nitrate? (b) How large are the chloride and iodate concentrations respectively in the solution? (c) What is the chloride concentration in the solution at the moment when silver iodate separates with the chloride on further addition of silver nitrate?

Ans. (a) $[Cl^-] + [IO_3^-] = 0.05$; (b) $[Cl^-] = 1.66 \times 10^{-4}$;
$[IO_3^-] = 4.98 \times 10^{-2}$; (c) $[Cl^-] = 1.67 \times 10^{-4}$.

8. A metal hydroxide $M(OH)_2$ which is a strong base has a solubility product equal to 4×10^{-15}. To 0.1 *M* solution of the metal salt sodium hydroxide is added. Assuming that the volume does not change, calculate the pH after precipitation (a) of 1 per cent of the metal, (b) of 50 per cent of the metal, (c) of 99 per cent of the metal.

Ans. (a) 7.30; (b) 7.45; (c) 8.30.

9. Calculate the solubility of silver chloride in a solution which is 1 *M* in ammonia and 0.1 *M* in sodium chloride.

$$S_{AgCl} = 10^{-10}; \quad \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]} = 7 \times 10^{-8}.$$

Ans. 1.21×10^{-2} *M*.

10. Calculate the solubility of silver bromide in a 1 *M* ammonia solution which is saturated with silver chloride.

$$S_{AgCl} = 10^{-10}; \; S_{AgBr} = 4.0 \times 10^{-13}$$

Ans. 1.5×10^{-4} *M*.

11. The following substances are to be precipitated: silver bromide, barium sulfate, calcium oxalate, barium iodate (iodic acid is a strong acid), zinc ammonium phosphate, magnesium hydroxide, calcium fluoride. In what cases is a quantitative precipitation likely to be obtained from acid medium?

CHAPTER VI

QUANTITATIVE SEPARATIONS

SEPARATIONS BY CHEMICAL METHODS

Fractional precipitation.

The general theory of fractional precipitation has been discussed in a previous chapter (p. 65). It was shown there that if two ions give slightly soluble compounds with the same reagent, the less soluble compound is precipitated first; and a separation is possible if the difference in the solubility products of the two compounds is sufficiently large. Theoretically, therefore, it is possible to predict by calculation whether a quantitative separation by fractional precipitation is possible. The result of such calculations should always be verified experimentally, since the ion giving the more soluble compound may be coprecipitated with the less soluble substance (compare the chapter on "Coprecipitation," p. 110).

A few separations based on fractional precipitation, which are important from the practical viewpoint, are discussed below in greater detail.

Separation of hydrous oxides.

If slightly soluble metal hydroxides (or better, hydrous oxides) are in equilibrium with the solution, the following relations hold:

$$\begin{aligned} &M(OH)_2 \qquad [M^{++}][OH^-]^2 = S_{M(OH)_2} && (1)\\ &M(OH)_3 \qquad [M^{+++}][OH^-]^3 = S_{M(OH)_3}. \end{aligned}$$

The system, metal hydroxide in equilibrium with a solution of the metal salt, exerts a buffer action (for definition of buffer see p. 44). From equation (1) we see that

$$[OH^-] = \sqrt{\frac{S_{M(OH)_2}}{[M^{++}]}} \qquad (2)$$

or

$$[H^+] = K_w\sqrt{\frac{[M^{++}]}{S_{M(OH)_2}}}. \qquad (3)$$

Addition of acid or base to the system metal ion-metal hydroxide results in a change of the metal-ion concentration in the solution, and consequently of the hydrogen-ion concentration. In the above case a hundredfold decrease of [M^{++}] corresponds to a tenfold decrease of the hydrogen-ion concentration. If the solubility product of the hydroxide is known, it is possible to calculate how much of the metal is left in the solution at any pH and also at what pH the precipitation can be considered to be quantitatively complete.

Britton[1] has given a list of the pH values at which various hydroxides are precipitated; his data are given in the following table.

TABLE XIV. pH AT WHICH VARIOUS HYDROXIDES ARE PRECIPITATED

pH	HYDROXIDE
11	Mg
9	Ag, Mn^{II}, La, Hg^{II}
8	Ce^{III}, Co, Ni, Cd, Pr, Nd, U^{VI}
7	Sm, Fe^{II} (?), Pb (?)
6	Zn, Be, Cu^{II}, Cr^{III}
5	Al
4	U^{IV}, Th
3	Sn^{II}, Fe^{III}, Zr

For various reasons we should be careful in the application of such data to quantitative separations of the hydrous oxides. In the first place, the data are not highly accurate. For example, Kolthoff and Kameda[2] found that zinc hydroxide begins to precipitate at a pH of 5.80 from 0.25 *M* zinc sulfate solutions, at a pH of 6.17 from 0.05 *M*, and at a pH of 6.5 from 0.01 *M* solutions. The precipitation, therefore, is far from complete at a pH of 6.

Moreover, the data obtained by Bowles and Partridge,[3] who made a study with the glass electrode in which they determined the pH at which precipitation of the rare-earth hydroxides began upon titration of a 0.01 *M* sulfate solution with 0.1 *N* sodium hydroxide at 25°, are not in quantitative agreement with those of Britton. They found for La^{+++} a pH of 7.61 (as chloride 8.03), for Ce^{+++} a pH of 7.07, for Nd^{+++} a pH of 6.73 (as chloride 7.40), for Pr^{+++} a pH of 6.98, for Yb^{+++} a pH of 6.16, for Th^{++++} a pH of 3.91, for Ce^{++++} a pH of 2.7.

In addition, the pH data depend upon the kind of anion present in the metal solution. If alkali hydroxide is added to a metal solution, the hydroxide separating out is not pure but is contaminated by anions. This coprecipitation may be attributed to an adsorption of the acid by the hydrous oxide or to a tendency of the latter to form basic salts. The higher the valence of the anion, the greater is its tendency to be coprecipitated. Sulfates, for example, are carried down to a much greater extent than chlorides. Organic ions particularly are strongly coprecipitated. Nevertheless, by a proper adjustment of the pH, it is possible to make satisfactory group separations. This can be done in acid medium in the presence of a proper buffer or in ammoniacal medium.

---

[1] H. T. S. Britton, J. Chem. Soc. *125*, 2124 (1927).

[2] I. M. Kolthoff and T. Kameda, J. Am. Chem. Soc. *53*, 832 (1931).

[3] J. A. C. Bowles and H. M. Partridge, Ind. Eng. Chem., Anal. Ed. *9*. 124 (1937).

Precipitation by ammonium hydroxide in the presence of ammonium salts. The alkaline earth hydroxides and magnesium hydroxide are not precipitated by ammonia if a sufficient amount of ammonium salt is present. The solubility product of magnesium hydroxide has the value 10^{-11} Therefore, no magnesium hydroxide will precipitate from a solution more dilute than 0.1 molar in magnesium at a pH of 9 or less than 9. The hydroxides of copper, zinc, nickel, and cobalt are precipitated by ammonia but dissolve in an excess of the latter with the formation of complex ammonio ions. Manganous hydroxide is not precipitated by ammonia, provided the solution contains a large excess of ammonium salt (the explanation is the same as for magnesium hydroxide). However, in alkaline medium the manganous ion is easily oxidized by the air, and on standing hydrous manganese dioxide separates. On the other hand, ferric iron, chromium, and aluminum are precipitated quantitatively under these conditions. The use of large amounts of ammonium salts is recommended in this separation. In the first place, an excess of an ammonium salt maintains the pH at a low value, thus decreasing the solubility of aluminum hydroxide (see p. 324). In the second place, a large excess of ammonium salt decreases the coprecipitation of cations such as calcium, magnesium, zinc, and nickel.

Separations with ammonia are open to objections from the quantitative viewpoint. The precipitated hydrous oxides are very gelatinous, difficult to filter and wash, and they have a strong tendency to adsorb other cations present in the solution. Very often a reprecipitation does not yield a pure precipitate, and the procedure is time-consuming owing to slow filtration and washing. However, the use of ammonia is of great practical importance (see chapter on "Rock Analysis," p. 737).

***Precipitation from acid medium at controlled* pH.** By proper adjustment of the pH of the solution it is possible to separate ferric iron, aluminum, and chromium from zinc, manganese, nickel, cobalt, and the alkaline earths. The adjustment of the pH is accomplished by the addition of a proper buffer agent. It is fairly simple to effect a quantitative precipitation of iron without precipitation of zinc, manganese, etc., since the former is quantitatively removed from the solution at a pH of 3. It is more difficult to find a pH at which aluminum and chromic chromium can be precipitated quantitatively without precipitating some of the other metals.

Various procedures have been described in the literature for the separation of the trivalent ions from the divalent in acid medium. One of the most popular is the basic-acetate method.

Basic-acetate method. In this procedure the pH of the medium is adjusted by the buffer acetic acid-ammonium acetate. In general, this procedure does not give very satisfactory results, since it is impossible to precipitate all the aluminum and chromium without partially precipitating zinc and other metals. The latter may partly precipitate as basic acetates or may be coprecipitated with the basic acetates of the trivalent metals. Therefore, one or more reprecipitations are usually required in order to get quantitative separations.

Other buffer systems have been used in place of acetic acid-ammonium acetate. Formic acid has an ionization constant about ten times larger than that of acetic acid; therefore, by using formic acid-formate buffers, the precipitation can be carried out at a lower pH. However, neither this system nor the succinic acid-succinate system gives satisfactory results in all cases. It has been found[1] that the combination benzoic acid-ammonium benzoate yields highly satisfactory results. With this system the precipitation of iron, aluminum, and chromium is quantitative at a pH of 3.8, and none of the divalent metals precipitate under the proper conditions. Even the coprecipitation of the latter is very small when the correct procedure is followed.

Various other methods have been described in which the pH of the medium is adjusted by the proper agents in order to precipitate the trivalent metals. This can be done, for example, by the addition of slightly soluble metal oxides, which, as we have seen, exert a buffer action when the corresponding metal ions are present in the solution. Zinc, magnesium, and mercuric oxides are used for this purpose. Carbonates, such as those of calcium, barium, cadmium, and lead, are used as well. Application of weak organic bases, such as aniline, pyridine,[2] hexamethylene tetramine,[3] and phenylhydrazine, has also been described for the same purpose. However, in general, all these are of subordinate importance in separations. Another method of adjusting the pH involves the addition of a reagent or a mixture of reagents which removes hydrogen ions. If an aluminum solution, for example, is boiled with sodium nitrite, the hydrogen ions formed by hydrolysis of the aluminum salt react with the nitrite to form nitrous acid, which decomposes and volatilizes on boiling, and aluminum hydroxide is precipitated:

---

[1] I. M. Kolthoff, V. A. Stenger, and B. Moskovitz, J. Am. Chem. Soc. *56*, 812 (1934).

[2] E. A. Ostraumow, Z. anal. Chem. *106*, 170, 244 (1936); Ann. chim. anal. chim. appl. *20*, 9 (1938); J. J. Lingane and H. Kerlinger, Ind. Eng. Chem., Anal. Ed. *13*, 77 (1941).

[3] See A. M. Ismail and H. F. Harwood, Analyst *62*, 185 (1937); T. Akiyama J. Pharm. Soc. Japan *56*, 893 (1936); *57*, 19 (1937).

$$AlCl_3 + 3\,NaNO_2 + 3\,H_2O \rightarrow Al(OH)_3 + 3\,NaCl + 3\,HNO_2\uparrow.$$

Similarly, sodium thiosulfate and potassium cyanate can be used:

$$Na_2S_2O_3 + 2\,H^+ \rightarrow H_2O + S + SO_2\uparrow + 2\,Na^+$$
$$KCNO + H^+ \rightarrow K^+ + HCNO\uparrow.$$

Mixtures of potassium iodide and iodate, bromide and iodate, or bromide and bromate can also be used for the removal of hydrogen ions:

$$IO_3^- + 5\,I^- + 6\,H^+ \rightarrow 3\,I_2 + 3\,H_2O$$
$$BrO_3^- + 5\,Br^- + 6\,H^+ \rightarrow 3\,Br_2 + 3\,H_2O.$$

Useful applications can be made of these reagents in various separations.[1] For the effect of acidity on the metal sulfides see p. 63.

Separations by complex formation.

Frequently use is made of the fact that the precipitation of an ion can be prevented by transforming it into a complex. The hydroxides of copper, zinc, cadmium, nickel, cobalt, and silver, for example, dissolve in an excess of ammonia with the formation of complex ammonio ions:

$$Ag^+ + 2\,NH_3 \rightleftharpoons Ag(NH_3)_2^+$$
$$Cu^{++} + 4\,NH_3 \rightleftharpoons Cu(NH_3)_4^{++}.$$

An application of this complex formation is made, for example, in the precipitation of iodide with silver in the presence of chloride. The relation between the stability constant of the complex on the one hand and the solubility products of silver iodide and of chloride on the other hand is such that all of the iodide will be precipitated, whereas the chloride remains in the solution (see p. 65).

A similar application of complex formation is made in the separation of iron from aluminum. Most organic acids containing hydroxyl groups form complexes with the di- and trivalent cations and prevent their precipitation as hydroxides. Thus, if we add alkali salts of tartaric acid, citric acid, salicylic acid, etc. to solutions of iron and aluminum (and divalent cations), the hydroxides do not precipitate on the addition of alkali. Iron can then be precipitated with ammonium sulfide (iron sulfide is extremely slightly soluble, see table on p. 64), whereas the aluminum remains in the solution because it does not form a sulfide.

---

[1] See L. Moser and W. Maxymowicz, Z. anal. Chem. *67*, 248 (1925).

Another application of complex formation may be made in the separation of calcium from relatively large amounts of magnesium by precipitation as calcium oxalate. Magnesium oxalate is relatively slightly soluble; however, its solubility increases with increasing excess of ammonium oxalate as a result of complex formation. Therefore, in the separation of calcium from magnesium a large excess of precipitating agent is often used to prevent precipitation of magnesium as oxalate (compare p. 356).

In volumetric analysis use is sometimes made of complex formation. Ferric ions, for example, have an oxidizing action. If these ions are transformed into a complex, their oxidizing effect is decreased. This can be done, for example, by the addition of fluoride, phosphate, or pyrophosphate. The yellow color of the solution disappears, since the complexes formed are colorless. Both ferric iron and cupric copper react quantitatively with potassium iodide to give an equivalent amount of iodine:

$$2\,Fe^{+++} + 2\,I^- \rightleftharpoons 2\,Fe^{++} + I_2$$
$$2\,Cu^{++} + 4\,I^- \rightleftharpoons 2\,CuI + I_2.$$

The sum of the two can be titrated iodometrically. In the presence of enough pyrophosphate and acid, or fluoride and hydrofluoric acid, only the copper reacts and can be titrated in the presence of the ferric complex.

Oxidation or reduction of one of the substances to be separated.

Many ions can exist in different states of oxidation, and this behavior can be made the basis of various separations. Trivalent chromium, for example, can be easily oxidized to chromate, which no longer precipitates with ammonia. Copper can be reduced to the cuprous state and precipitated as cuprous thiocyanate. An effective separation of copper from iron is obtained in this manner.

Iron and aluminum can be separated by reducing the iron to the ferrous state. Ferrous hydroxide is a much stronger base than ferric hydroxide and does not precipitate when the pH is less than 6. If sodium thiosulfate is added to the mixture of iron and aluminum and the solution boiled, ferric iron is reduced to the ferrous state and aluminum is quantitatively precipitated:

$$AlCl_3 + 3\,H_2O \rightleftarrows Al(OH)_3 + 3\,H^+ + 3\,Cl^-$$
$$S_2O_3^= + 2\,H^+ \rightarrow SO_2 + S + H_2O.$$

The precipitate consists of a mixture of hydrous aluminum oxide and sulfur which can be filtered and washed fairly easily and ignited to the oxide.

In the separation of cobalt and nickel use can be made of the fact that both form soluble complexes with an excess of potassium cyanide. The cobaltous (Co^{II}) complex is easily oxidized to the corresponding complex of Co^{III}, which is so stable that it does not react with any of the ordinary reagents for cobalt. The nickel complex remains unchanged, and the nickel can then be precipitated by means of various reagents.

Organic precipitants.[1]

Various organic reagents combine with inorganic ions or compounds to form slightly soluble products in which the metal is no longer present in the ionic state but is held by covalence forces. Such compounds are called coördination compounds. Usually they are distinguished by slight solubility in water and often by their intense color. In organic solvents the compounds are as a rule more soluble than in water.

Often in gravimetric and colorimetric analysis, and occasionally in volumetric, the formation of such coördination compounds is applied. An advantage of these compounds, besides the low solubility in aqueous medium, is the usually high molecular weight; therefore a small amount of the ion sought may yield a relatively large amount of precipitate. Many analytical studies have been made during recent years in which new organic reagents for metals are described. There is still a wide field left for exploration; one of the chief aims of the analytical chemist is the finding of specific reagents for each element. This would mean that an element could be determined in the presence of any other by the application of the specific reagent. In a few cases this ideal has been approached. Usually, however, organic compounds react with a group of metals; these are called group reagents and are useful in the separation of the elements into groups. In some cases certain elements which react with such a group reagent can be made inactive by transforming them into complexes so that more specific separations can be made.

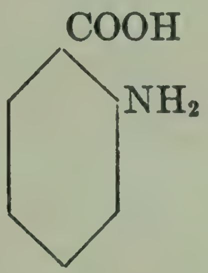
---

[1] For general reviews of the application of organic reagents to the detection and quantitative (gravimetric, volumetric, and colorimetric) determination of inorganic ions or compounds see:

F. Feigl, *Qualitative Analysis by Spot Tests; Vol. I, Theoretical Part (1940); Vol. II, Practical Part (1939);* Elsevier Publishing Co., Inc., New York. W. Prodinger, *Organic Reagents Used in Quantitative Inorganic Analysis*, translated by S. Holmes, Elsevier Publishing Co., Inc., New York, 1940. J. H. Yoe and L. A. Sarver, *Organic Analytical Reagents*, John Wiley and Sons, New York, 1941. Paul von Stein, *Organic Reagents in Inorganic Analysis*, Chemical Publishing Co., Brooklyn, 1942. I. Mellan, *Organic Reagents in Inorganic Analysis*, P. Blakiston's Son and Co., Philadelphia, 1941. *Organic Reagents for Metals and for Certain Acid Radicals*, by the Staff of Hopkins and Williams Ltd., London, 4th ed., 1940.

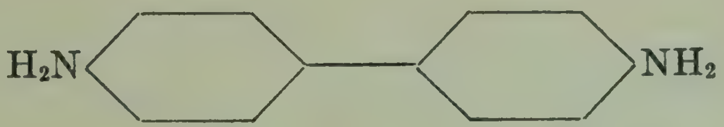
The general properties of some important organic precipitants are described below.

Anthranilic acid.



A solution of the sodium salt of anthranilic acid precipitates zinc, cobalt, nickel, cadmium, copper, lead, and mercuric mercury[1] from neutral or weakly acidic solutions. The crystalline precipitates filter easily and can be weighed after drying at 105° to 110°. The anthranilic acid in the precipitates can also be determined volumetrically by treatment with an acid bromate-bromide mixture. The excess of bromine is back-titrated iodometrically. One molecule of anthranilic acid reacts with six atoms of bromine.

Benzidine.

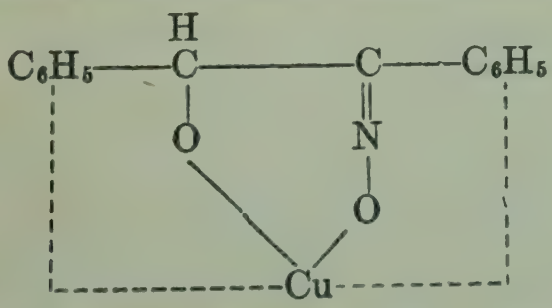


Benzidine hydrochloride yields a white, crystalline precipitate with sulfate. The precipitate can be weighed, or titrated with standard sodium hydroxide with phenolphthalein as indicator. The liberated benzidine is slightly soluble and is such a weak base that its saturated solution does not turn phenolphthalein pink.

Benzoin oxime (Cupron).

$$C_6H_5—CHOH—C{=}NOH—C_6H_5$$

According to Feigl[2] the acyloin oximes are specific reagents for copper. The benzoin oxime yields a green, slightly soluble copper compound:



---

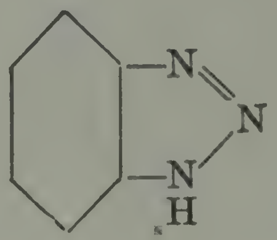
[1] H. Funk and M. Ditt, Z. anal. Chem. *91*, 332 (1933); *93*, 241 (1933); *96*, 385 (1934).

[2] F. Feigl, Ber. *56*, 2083 (1923); Mikrochem. *1*, 76 (1923).

The precipitation is carried out in ammoniacal medium. Ions which are precipitated by ammonia can be kept in solution by the addition of sodium potassium tartrate. Ephraim[1] recommends the use of salicylaldoxime in place of α-benzoin oxime. H. B. Knowles[2] makes use of α-benzoin oxime in the determination of molybdenum (see p. 727).

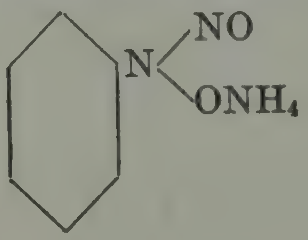
Flagg and Furman[3] showed that under the proper conditions bismuth and zinc can be precipitated quantitatively with salicylaldoxime.

Benzotriazole.



This compound has been recommended[4] for the precipitation of copper from ammonium tartrate-acetate medium (pH 7.0 to 8.5). However, silver, nickel, cadmium, zinc, cobalt, and ferrous iron are also precipitated.

Ammonium salt of nitrosophenylhydroxylamine (Cupferron).



This reagent was introduced by Baudisch[5] for the separation of copper from iron. It gives slightly soluble salts with various metal ions in which the ammonium is replaced by the metal. The precipitates are not weighed as such but ignited to the metal oxides. It is a valuable reagent in quantitative analysis because the precipitation may be carried out in strongly acid media. It provides complete separation of elements such as iron, vanadium, zirconium, titanium, tin, columbium, and tantalum from others such as aluminum, beryllium, phosphorus, manganese, nickel, and sexivalent uranium. For further details the reader is referred to the comprehensive section on this reagent in *Applied Inorganic Analysis* by Hillebrand and Lundell[6] and to a monograph by Smith.[7]

---

[1] F. Ephraim, Ber. *64*, 1210, 1215 (1931); W. Reif, Mikrochem. *9*, 424 (1931); for micro palladium determination see H. Holzer, Z. anal. Chem. *95*, 392 (1933).

[2] H. B. Knowles, Bur. Standards J. Research *9*, 1 (1932).

[3] J. F. Flagg and N. H. Furman, Ind. Eng. Chem., Anal. Ed. *12*, 663 (1940).

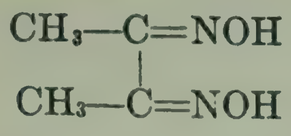
[4] J. A. Curtis, Ind. Eng. Chem., Anal. Ed. *13*, 349 (1941).

[5] O. Baudisch, Chem. Ztg. *33*, 1298 (1909).

[6] W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*, pp. 109–112 (1929). See also G. E. F. Lundell and H. B. Knowles, J. Ind. Eng. Chem. *12*, 344 (1920).

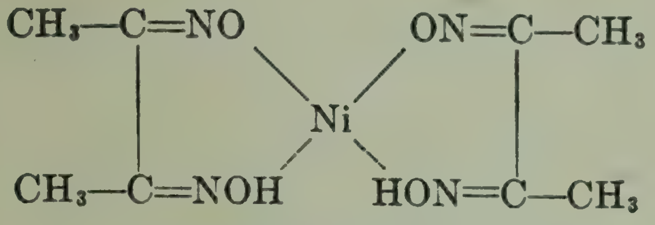
[7] G. F. Smith, "Cupferron and Neo-Cupferron," G. Frederick Smith Chemical Co., Columbus, Ohio (1938).

Dimethylglyoxime (*Diacetyldioxime*).[1]



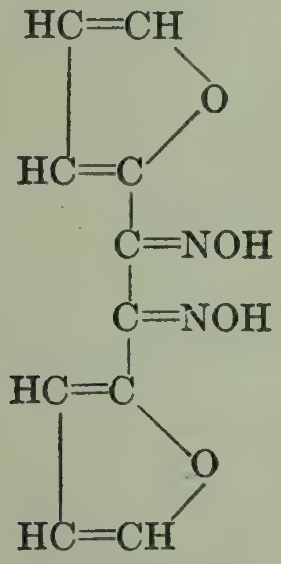
$$\begin{array}{l} CH_3\text{—}C{=}NOH \\ \quad\;\;| \\ CH_3\text{—}C{=}NOH \end{array}$$

This reagent was first synthesized by Tschugaeff,[2] who recommended it for the detection of nickel, and two years later it was applied by Brunck [3] to the determination of nickel in steel. With nickel solutions it gives a bright-red precipitate:



(--- denotes a coördinate bond)

If the precipitation is made at a pH less than 5, palladium is the only other element which gives a slightly soluble coördination compound with the oxime. The reagent itself is only slightly soluble in water and is used in the form of a 1 to 2 per cent solution in alcohol. A large excess of the reagent added to the aqueous nickel solution may precipitate and contaminate the nickel dimethylglyoxime. Methylbenzoylglyoxime [4] has also been recommended as a reagent for nickel and palladium. Soule [5] recommends α-furil dioxime instead of dimethylglyoxime.



α-furil dioxime

It has two advantages over diacetyldioxime. α-Furil dioxime is more soluble in water, and the nickel compound contains only 11.81 per cent of nickel (nickel dimethylglyoxime contains 20.31 per cent of the metal).

---

[1] An excellent review with a bibliography of the applications of the dioximes to analytical chemistry is given by H. Diehl in a monograph published by the G. Frederick Smith Chemical Co., Columbus (Ohio), 62 pp., 1940.

[2] L. Tschugaeff, Ber. *38*, 2520 (1905); Z. anorg. Chem. *46*, 144 (1905).

[3] O. Brunck, Z. angew. Chem. *20*, 834 (1907).

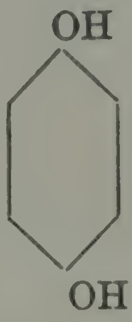
[4] J. Hanus, A. Jélek, and J. Lukas, Chem. News, *131*, 401 (1925); H. Holzer, Z. anal. Chem. *95*, 392 (1933).

[5] B. A. Soule, J. Am. Chem. Soc. *47*, 981 (1925). α-Benzil dioxime has been recommended by F. W. Atack, Chem. Ztg. *37*, 773 (1913); Analyst *38*, 316 (1913).

Hexanitrodiphenylamine (Dipicrylamine).

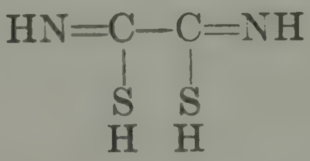
The magnesium or sodium salt of this reagent yields a slightly soluble, red, crystalline precipitate with potassium solutions. Use is made of this precipitation in the gravimetric and colorimetric determination of potassium.[1]

Hydroquinone.



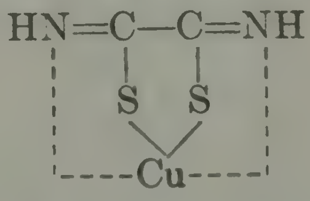
In hot acid solution gold is reduced and quantitatively precipitated as the metal by hydroquinone.[2] Platinum and palladium do not interfere.

Hydrorubeanic acid.



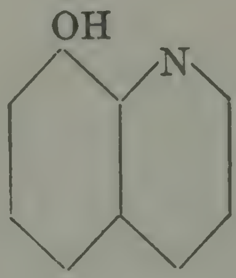
$$\begin{array}{cccc} HN= & C & - & C=NH \\ & | & & | \\ & S & & S \\ & H & & H \end{array}$$

An alcoholic solution of hydrorubeanic acid gives quantitative precipitation of copper, nickel, and cobalt[3] in ammoniacal or slightly acid solutions. The copper precipitate is black and has the composition



The precipitate with nickel is blue or blue-violet; cobalt yields a brown amorphous precipitate. All of these precipitates are extremely slightly soluble.

8-Hydroxyquinoline (Oxine).



Oxine was introduced as a reagent in quantitative analysis by Berg[4] and has since become a valuable reagent for the determination and separation of various metals. It forms compounds with the metals in which the hydrogen of the hydroxyl group is replaced by an equivalent of the metal:

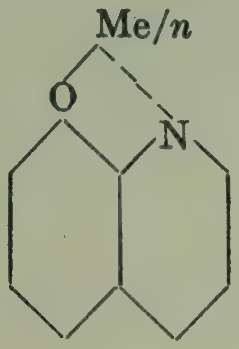
---

[1] Cf. I. M. Kolthoff and G. H. Bendix, Ind. Eng. Chem., Anal. Ed. *11*, 94 (1939).

[2] F. E. Beamish, J. J. Russell, and J. Seath, Ind. Eng. Chem., Anal. Ed. *9*, 174 (1937).

[3] P. Ray and R. M. Ray, J. Indian Chem. Soc. *3*, 118 (1926); Ray and H. Dhar. *ibid.* *5*, 497 (1928); P. Ray, Z. anal. Chem. *79*, 94 (1929).

[4] R. Berg, Z. anal. Chem. *70*, 341; *71*, 23, 171, 321, 369 (1927); *72*, 177 (1927); *76*, 191 (1929); and especially R. Berg, "Das o-Oxychinolin (Oxin)," Vol. XXXIV in series of *Die Chemische Analyse*, F. Enke, Stuttgart, 1936.



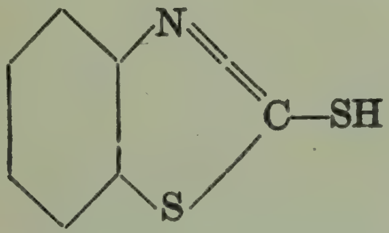
Me/n denotes an equivalent of the metal. Copper, bismuth, cadmium, aluminum, ferric iron, nickel, cobalt, zinc, manganese, titanium, and thorium are quantitatively precipitated from hot acetic acid-acetate solution. Magnesium is precipitated from ammoniacal medium. In the latter case large amounts of calcium may interfere. Aluminum may be quantitatively separated from magnesium and beryllium by precipitation in acetic acid-acetate medium. Various metals are also quantitatively precipitated from alkaline solutions (sodium hydroxide or ammonia) in the presence of sodium potassium tartrate, the latter serving to prevent the precipitation of metal hydroxides.

The metal hydroxyquinolates can be weighed as such after drying. Ignition to the metal oxide does not yield good results in some cases, since part of the metal volatilizes as the metal oxine. This can be prevented by the addition of oxalic acid or sulfuric acid before the ignition. Small amounts of the metal are better determined volumetrically with potassium bromate as standard solution instead of gravimetrically (see practical part, p. 587 and p. 638).

The table on pages 80–81 gives a summary of the determination of various elements with oxine.

5-7-Dibromohydroxyquinoline. This reagent precipitates copper [1] and ferric iron [2] from mineral acid medium.

Mercaptobenzthiazole.



According to Spacu and Kuras [3] copper, bismuth, lead, mercury, silver, gold, and thallium form insoluble precipitates with mercaptobenzthiazole. Cadmium is precipitated in ammoniacal medium, yielding a yellow precipitate. The reagent is suitable for the separation of copper from cadmium, as the former is precipitated in acid medium.

---

[1] L. W. Haase, Z. anal. Chem. *78*, 113 (1929).

[2] R. Berg and H. Küstenmacher, Z. anorg. allgem. Chem. *204*, 215 (1932).

[3] G. Spacu and M. Kuras, Z. anal. Chem. *102*, 24, 108 (1935).

TABLE XV. THE METAL HYDROXYQUINOLATES

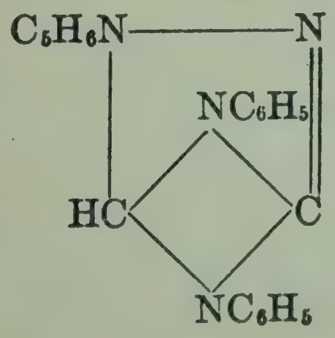
METAL	FORMULA	pH RANGE FOR COMPLETE PRECIPITATION [a]	REFERENCES
Aluminum	$Al(C_9H_6ON)_3$ (100–160°)	4.2–9.8	R. Berg, Z. anal. Chem. *71*, 369 (1927); I. M. Kolthoff and E. B. Sandell, J. Am. Chem. Soc. *50*, 1900 (1928); G. E. F. Lundell and H. B. Knowles, Nat. Bur. Standards J. Research *3*, 91 (1929); R. Lang and J. Reifer, Z. anal. Chem. *93*, 162 (1933); T. Heczko, Chem. Ztg. *58*, 1032 (1934); R. C. Chirnside, C. F. Pritchard, and H. P. Rooksby, Analyst *66*, 399 (1941).
Antimony	$Sb(C_9H_6ON)_3$ (110°) $SbO \cdot C_9H_6ON \cdot (C_9H_7ON)_2$	*ca.* 6 (Pirtea) Tartrate solution	T. I. Pirtea, Z. anal, Chem. *118*, 26 (1939).
Bismuth	$Bi(C_9H_6ON)_3 \cdot H_2O$ (100°) $Bi(C_9H_6ON)_3$ (130–140°)	4.8–10.5	R. Berg, Z. anal. Chem. *72*, 177 (1927).
Cadmium	$Cd(C_9H_6ON)_2 \cdot 2\,H_2O$ (R. T.) $Cd(C_9H_6ON)_2$ (130°)	5.4– > 13	R. Berg, Z. anal. Chem. *71*, 321 (1927).
Calcium		9.2– > 13	
Cerium	$Ce(C_9H_6ON)_3$ (110°)	Ammoniacal tartrate solution	R. Berg and E. Becker, Z. anal. Chem. *119*, 1(1940).
Columbium	Uncertain	Approx. neutral oxalate-acetate solution	P. Süe, Compt. rend. *196*, 1022 (1933).
Chromium (Cr^{III})	$Cr(C_9H_6ON)_3$ (110°)	NaOH + NH_4 acetate soln. (pptn. not quite complete)	E. Taylor-Austin, Analyst *63*, 710 (1938).
Cobalt	$Co(C_9H_6ON)_2 \cdot 2\,H_2O$ (R. T.) $Co(C_9H_6ON)_2$ (130°)	4.2–11.6 4.3–14.5 (F. & W.)	R. Berg, Z. anal. Chem. *76*, 195 (1929).
Copper	$Cu(C_9H_6ON)_2$ (110°)	2.7– > 13 5.3–14.6 (F. & W.)	R. Berg, Z. anal. Chem. *70*, 341 (1947).
Gallium	$Ga(C_9H_6ON)_3$ (110–150°)	*ca.* 6-8 (Geilmann)	W. Geilmann and F. W. Wrigge, Z. anorg. allgem. Chem. *209*, 129 (1932).
Indium	$In(C_9H_6ON)_3$ (120°)	Acetic acid-acetate	See Gallium.
Iron	$Fe(C_9H_6ON)_3$ (100–160°)	2.8–*ca.* 12	R. Berg, Z. anal. Chem. *76*, 191 (1927); H. V. Moyer and W. R. Remington, Ind. Eng. Chem., Anal. Ed. *10*, 212 (1938) (separation from Al in tartrate solution).
Lead		8.4–12.3	
Magnesium	$Mg(C_9H_6ON)_2 \cdot 2\,H_2O$ (105°) $Mg(C_9H_6ON)_2$ (135°)	8.2– > 13 9.4–12.7 (F. & W.)	R. Berg, Z. anal. Chem. *71* 23, 122 (1927) H. V. Moyer and W. R Remington, Ind. Eng Chem., Anal. Ed. *10*, 212 1938; J. Redmond and H. Bright, Bur. Standards J. Research *6*, 113 (1931) Redmond, *ibid.* *10*, 823 (1933). Also see p. 373.

---

[a] The pH values given are those of H. Goto (J. Chem. Soc. Japan *54*, 725 (1933); *56*, 314 (1935)) unless otherwise indicated The values identified by (F. & W.) or (F.) were obtained by H. R. Fleck and A. M. Ward (Analyst *58*, 3888 (1933)) and H. R. Fleck (Analyst *62*, 378 (1937))

Metal	Formula	pH Range for Complete Precipitation	References
Manganese	$Mn(C_9H_6ON)_2 \cdot 2\,H_2O$ (R. T.) $Mn(C_9H_6ON)_2$ (110°)	5.9–10.0	R. Berg, Z. anal. Chem. *76*, 195 (1929).
Molybdenum	$MoO_2(C_9H_6ON)_2$ (130°)	3.6–7.3 (F. & W.)	G. Balanescu, Ann. chim. anal. appl. [2] *12*, 259 (1930); Z. anal. Chem. *83*, 470 (1931).
Nickel	$Ni(C_9H_6ON)_2 \cdot 2\,H_2O$ (R. T.) $Ni(C_9H_6ON)_2$ (130°)	4.6–10.0 4.3–14.6 (F. & W.)	R. Berg, Z. anal. Chem. *76* 195 (1929).
Palladium	$Pd(C_9H_6ON)_2$ (110°)	Dil. HCl soln.	Treadwell, *Tabellen und Vorschriften zur quantitativen Analyse*, p. 61.
Thorium	$Th(C_9H_6ON)_4 \cdot (C_9H_7ON)$ (110°)	4.4–8.8	F. J. Frere, J. Am. Chem. Soc. *55*, 4362 (1933); F Hecht and W. Ehrmann, Z. anal. Chem. *100*, 98 (1935).
Titanium	$TiO(C_9H_6ON)_2$ (110°)	4.8–8.6	R. Berg and M. Teitelbaum, Z. anal. Chem. *81*, 1 (1930).
Tungsten	$WO_2(C_9H_6ON)_2$ (120°)	5.0–5.7	S. Halberstadt, Z. anal. Chem. *92*, 86 (1932); J. A. Merz, Svensk Kem. Tid. *53*, 400 (1941).
Uranium	$UO_2(C_9H_6ON)_2 \cdot (C_9H_7ON)$ (110°)	4.1–8.8 5.7–9.8 (F. & W.)	F. Hecht and W. Reich-Rohrwig, Monatsh. *53-54*, 596 (1929).
Vanadium		Acetic acid-acetate	A. Jilek and V. Vicovsky Collection Czech. Chem Commun. *4*, 1 (1932); R. Montequi and M Gallego, Anales Soc. españ. fís. quim. *32*, 134 (1934).
Zinc	$Zn(C_9H_6ON)_2 \cdot 2\,H_2O$ (98°) $Zn(C_9H_6ON)_2$ (110°–160°)	4.4–> 13 4.6–13.4 (F. & W.)	R. Berg, Z. anal. Chem. *71*, 171 (1927); H. V. Moyer and W. R. Remington, Ind. Eng. Chem., Anal. Ed. *10*, 212 (1938).
Zirconium	$Zr(C_9H_6ON)_4$ (140°)	Acetic acid-acetate	P. Süe and G. Wétroff, Bull. soc. chim. [5] *2*, 1002 (1935); G. Balanescu, Z. anal. Chem. *101*, 101 (1935).

Nitron. Diphenyl-endo-anilo hydro-triazole.



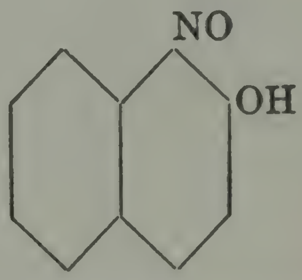
This reagent is a strong base; it precipitates nitrates as the slightly soluble crystalline nitron nitrate,[1] $C_{20}H_{16}N_4 \cdot HNO_3$. The solubility of the latter in

[1] M. Busch, Ber. *38*, 861 (1905); A. Gutbier, Z. angew. Chem. *18*, 494 (1905).

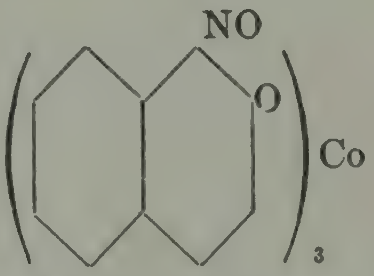
very dilute sulfuric acid at 20° amounts to 10 mg. of salt per 100 ml. of saturated solution, which is equivalent to 1.7 mg. HNO_3. Nitron is used in the form of a 10 per cent solution in 5 per cent acetic acid, and the precipitation is made from solutions slightly acidified with sulfuric acid.

The following acids also form slightly soluble salts with nitron and interfere with the determination: perchloric, hydriodic, thiocyanic, chromic, chloric, nitrous, and hydrobromic.

α-Nitroso-β-naphthol.



This reagent precipitates the following elements from slightly acid solutions: copper, uranium, chromium, zirconium, titanium, vanadium, tin, tungsten, palladium, iron, and cobalt. These metals may be quantitatively separated from antimony, aluminum, manganese, nickel, zinc, magnesium, calcium, barium, and strontium.[1] Cobalt is oxidized to the trivalent state by the reagent and then precipitated as



Recent investigations in this laboratory make it doubtful whether cobalt is in the trivalent state in the precipitate.

The most important application of α-nitroso-β-naphthol is made in the determination of cobalt in the presence of large amounts of nickel. A solution of the reagent in 50 per cent acetic acid is added to the nickel-cobalt solution, which is acidified with hydrochloric acid. After washing, the brick-red precipitate is ignited in air and weighed as Co_3O_4 or, better, reduced to metallic cobalt in hydrogen.

Phenylarsonic acid.

$$C_6H_5AsO(OH)_2$$

This reagent is used for the determination of zirconium[2] and tin.[3] It may be used for the determination of zirconium in steels.[4] Titanium, chromium, nickel, copper, vanadium, thorium, and molybdenum do not interfere, but tin is partially precipitated. *n-Propylarsonic acid* has been shown[5] to be a satisfactory reagent for the determination of zirconium in the presence of a number of other elements, including tin. *p-Hydroxyphenylarsonic acid*[1] precipitates titanium and zirconium quantitatively in dilute mineral acid solutions. Cerium, tin, and phosphate interfere. In the presence of hydrogen peroxide titanium is not precipitated. Chandelle[2] uses *disodium methylarsinite* (arrhenal) for the determination of zirconium.

---

[1] G. Knorre, Z. angew. Chem. *17*, 677 (1904); for separation of Pd from Pt see W. Schmidt, Z. anorg. allgem. Chem. *80*, 335 (1913); F. Krauss and H. Dencke, Z. anal. Chem. *67*, 86 (1925); C. Mayr, Z. anal. Chem. *98*, 402 (1934).

[2] A. C. Rice, H. C. Fogg, and C. James, J. Am. Chem. Soc. *48*, 895 (1926).

[3] J. S. Knapper, K. A. Craig, and G. C. Chandlee, J. Am. Chem. Soc. *55*, 3945 (1933).

[4] H. H. Geist and G. C. Chandlee, Ind. Eng. Chem., Anal. Ed. *9*, 169 (1937).

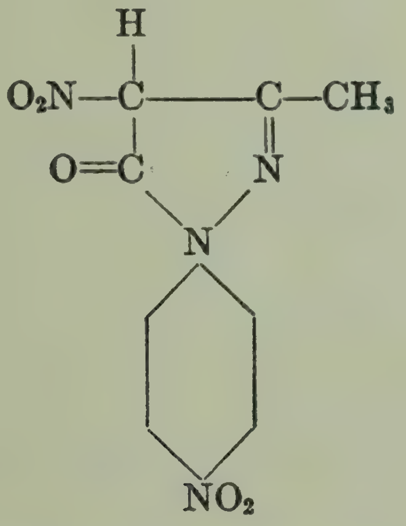
[5] F. W. Arnold and G. C. Chandlee, J. Am. Chem. Soc. *57*, 8 (1935).

Phenyl thiohydantoic acid.

$$C_6H_5NC(NH_2)SCH_2COOH$$

This reagent was used by Willard and Hall[3] for the quantitative precipitation of cobalt from ammoniacal medium. The compound with cobalt contains a large amount of water and has no definite composition; the cobalt is determined by ignition to Co_3O_4. By means of this reagent cobalt can be separated from aluminum, chromium, vanadium, uranium, tungsten, molybdenum, arsenic, titanium, zinc, manganese, calcium, and magnesium. Nickel is partially precipitated, but the precipitate is soluble in concentrated ammonia.

Picrolonic acid.



Picrolonic acid forms slightly soluble salts with a number of metals. The reagent is especially suitable for the determination of calcium,[4] lead,[5] and thorium.[6]

Pyridine. Pyridine forms insoluble complexes[7] with zinc, manganese, cadmium, nickel, cobalt, and copper thiocyanates of the general formula:

$$M(CNS)_2 \cdot (\text{Pyridine})_2.$$

Alkali thiocyanate and pyridine are added to the neutralized metal solution. The complex pyridine salts form crystalline precipitates which are easily filtered and washed with an aqueous pyridine solution.

---

[1] C. T. Simpson and G. C. Chandlee, Ind. Eng. Chem., Anal. Ed. *10*, 642 (1938).

[2] R. Chandelle, Bull. soc. chim. Belg. *46*, 423 (1937).

[3] H. H. Willard and D. Hall, J. Am. Chem. Soc. *44*, 2219, 2226, 2237, 2253 (1922).

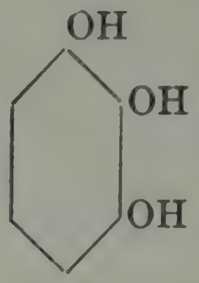
[4] R. Dworzak and W. Reich-Rohrwig, Z. anal. Chem. *86*, 98 (1931).

[5] F. Hecht, W. Reich-Rohrwig, and H. Brantner, *ibid. 95*, 152 (1933).

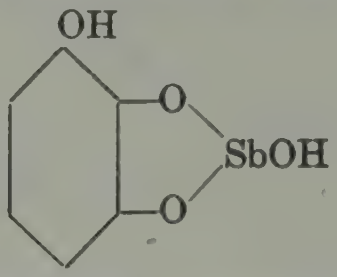
[6] F. Hecht and W. Ehrmann, *ibid. 100*, 87 (1935).

[7] G. Spacu and J. Dick, Z. anal. Chem. *71*, 97, 442 (1927); *74*, 188 (1928); *76*, 273 (1929).

Pyrogallol.

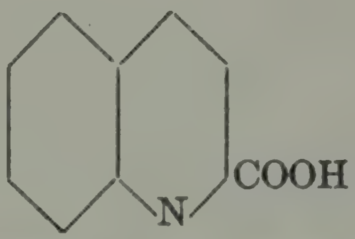


Pyrogallol forms crystalline, insoluble, complex salts with antimony[1] and bismuth[2] and can be used as a reagent for the quantitative determination of these metals. The antimony precipitate has the composition:

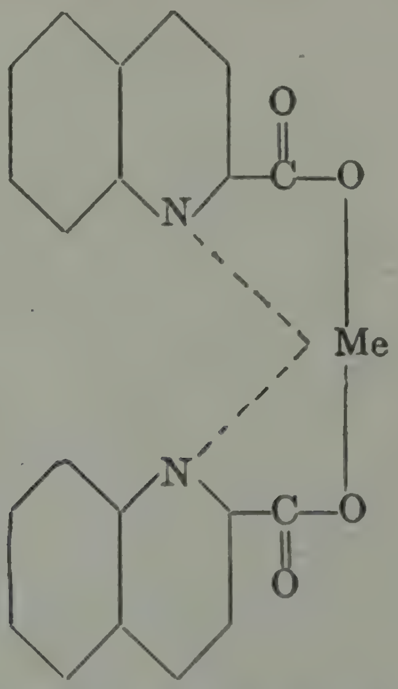


The bismuth compound has a similar composition.

Quinaldinic acid.



According to investigations of P. Ray and M. K. Bose[3] quinaldinic acid gives quantitative precipitations with copper, cadmium, zinc, ferrous iron, and uranyl ions:



Ferrous salts yield a dark-red precipitate, which on standing is transformed into an isomeric blue compound. The reaction is very sensitive (less than

---

[1] F. Feigl, Z. anal. Chem. *64*, 41 (1924).

[2] F. Feigl and H. Ordelt, *ibid.* *65*, 448 (1924).

[3] P. Ray and M. K. Bose, Z. anal. Chem. *95*, 400 (1934), *100*, 324 (1935); Mikrochem. *17*, 11 (1935); P. Ray and J. Gupta, *ibid.* *17*, 14 (1935), *18*, 89 (1935).

0.1 mg. Fe^{++} per liter) and may be used for the colorimetric determination of ferrous iron. Ferric salts give an amorphous yellow precipitate which is fairly soluble in mineral acid. Copper is precipitated from hot acidified solution; the precipitate has the composition $(C_{10}H_6NO_2)_2Cu \cdot H_2O$ after drying at 125° (14.96 per cent copper). Cadmium, manganese, and cobalt are not precipitated from dilute sulfuric acid, and copper can be quantitatively determined in the presence of these metals. The precipitation is made from hot acetic acid solution in the presence of phosphoric, arsenic, and arsenious acids. The cadmium salt of quinaldinic acid is soluble in mineral acid. Cadmium is precipitated from hot weakly acid medium and the solution neutralized with ammonia or sodium hydroxide. The precipitate contains no water after drying at 125° C.

Zinc is quantitatively precipitated from dilute acetic acid solution at room temperature. After drying at 125° C. the precipitate contains one molecule of water. Manganese, magnesium, barium, and calcium do not give precipitates under the above conditions, and a quantitative separation of zinc from these cations can be obtained. Uranyl ion is precipitated from a hot solution containing a large amount of ammonium chloride; the precipitate is finally ignited and weighed as U_3O_8.

Various other metals, such as mercury, lead, silver, nickel, manganese, aluminum, and chromium, yield slightly soluble compounds with the quinaldinic acid. The latter, therefore, is a highly unspecific reagent.

Tannin. Tannin is a valuable reagent for the separation of certain of the rarer elements. It has been used by Powell and Schoeller for the separation of tantalum and columbium,[1] and the separation of these from zirconium, thorium, and aluminum.[2] It is also possible to separate titanium from zirconium,[3] and uranium from tantalum, columbium, and titanium [4] with this reagent. Tannin precipitates aluminum but not beryllium in an acetate solution, and the two elements can thus be separated.[5] It is also possible to effect a separation of gallium [6] from zinc, nickel, cobalt, manganese, cadmium, beryllium, and thorium by the use of tannin.

Tetraphenylarsonium chloride $(C_6H_5)_4AsCl$. This is a reagent for mercury, tin, cadmium, zinc, and various anions.[7]

Thioglycolic β-amino naphthalide (Thionalide).

$$\beta\text{-}C_{10}H_7NHCOCH_2SH$$

According to Berg and Roebling [8] thionalide forms slightly soluble compounds with most metals of the hydrogen sulfide group. Use is made of this fact in the gravimetric, volumetric (iodometric), colorimetric, and nephelometric determination of these metals. From dilute mineral acid solution copper, silver, gold, mercury, tin, arsenic, antimony, bismuth, platinum, and palladium precipitate. From acetic acid or buffered solutions the following metals are also precipitated: cadmium, lead, cobalt, manganese, and thallium (I). From ammoniacal solution containing cyanide and tartrate only thallium is precipitated. The precipitates can be weighed as such. If it is desired to weigh after ignition, the thionalide is decomposed with nitric or sulfuric acid. The reagent can also be used in the volumetric determination of the metals. Dilute solutions can be titrated with a standard solution of the reagent until upon further addition no precipitate occurs. The iodometric titration is more accurate. After solution of the washed precipitate in a suitable solvent, the solution is titrated with standard iodine solution. The —SH group of the reagent is oxidized to the —RS—SR— group:

---

[1] A. R. Powell and W. R. Schoeller, Analyst *50*, 485 (1925); W. R. Scholler, *ibid.* *57*, 750 (1932); Schoeller, *The Analytical Chemistry of Tantalum and Niobium.*

[2] W. R. Schoeller and E. F. Waterhouse, Analyst *53*, 515 (1928); W. R. Schoeller and A. R. Powell, *ibid.* *57*, 550 (1932).

[3] A. R. Powell and W. R. Schoeller, Analyst *55*, 605 (1930).

[4] W. R. Schoeller and H. W. Webb, Analyst *58*, 143 (1933).

[5] L. Moser and M. Niessner, Monatsh. *48*, 113 (1927); L. Moser and J. Singer, *ibid.* *48*, 673 (1927).

[6] L. Moser and A. Brukl, Monatsh. *50*, 657 (1928).

[7] H. H. Willard and G. M. Smith, Ind. Eng. Chem., Anal. Ed. *11*, 186, 269 (1939).

[8] R. Berg and W. Roebling, Ber. *68*, 403 (1935); see also R. Berg, Angew. Chem. *23*, 404 (1934); Z. anal. Chem. *109*, 305 (1937); *112*, 161 (1938).

$$I_2 + 2\,RSH \rightarrow RS{-}SR + 2\,H^+ + 2\,I^-.$$

Traces of metals can be determined colorimetrically or nephelometrically. In the colorimetric determination the precipitate is dissolved in methanol or acetone and treated with an excess of phosphomolybdate or phosphotungstate. The blue color is compared with that obtained with a standard solution of the reagent. In the nephelometric determination the turbid solutions obtained upon the addition of reagent are compared with those obtained with standard solutions of the metals.

From alkaline solutions (0.2 *N* sodium hydroxide) containing tartrate only the following metals are precipitated: copper, silver, gold, mercury, cadmium and thallium. Trivalent iron does not interfere as it forms a soluble complex with tartrate which does not oxidize the reagent. From a tartrate solution in 0.2 *N* sodium carbonate gold, thallium, tin, lead, antimony, and bismuth are precipitated.

SEPARATIONS BY PHYSICAL METHODS

Distillation or volatilization.

The compound to be determined is volatile or can be transformed into a volatile compound. Upon distillation of the mixture it can be determined in the distillate, or it can be absorbed in a suitable reagent. The water content of a solid, for example, can be determined directly by absorbing the water given off on heating in some suitable drying agent and determining the increase in weight, or indirectly if no other constituents are volatilized. In the direct determination of carbon dioxide the gas evolved on addition of acid to the sample is first dried and then absorbed by a suitable alkaline substance, and the increase in weight of the alkali is determined. An alternative method consists in absorbing the gas in an excess of standard barium hydroxide solution. The excess of barium hydroxide is then titrated back with standard acid. The distillation method also finds application in the determination of other acids which are volatile, such as formic acid and its homologues. In the determination of ammonium salts the solution made alkaline with sodium hydroxide is distilled, and the evolved ammonia is absorbed in a known excess of standard acid (see p. 562). Use is made of this method in the determination of nitrogen in organic compounds. By decomposition of the sample with sulfuric acid in the presence of a catalyst, the nitrogen is transformed into ammonium sulfate (p. 565).

Arsenic can be separated from many other metals by distillation as $AsCl_3$. Boron can be transformed into the volatile methyl borate, $B(OCH_3)_3$, by distilling the sample with concentrated sulfuric acid and methyl alcohol, and determined in the distillate. Fluorine can be distilled in the form of hydrogen fluoride if platinum apparatus is used. From glass apparatus it can be quantitatively distilled as H_2SiF_6 after mixing with quartz powder, or from concentrated sulfuric acid in the form of SiF_4. Some oxidizing agents can be determined by a distillation in acid medium in the presence of an excess of iodide, bromide, or chloride (see p. 616). The halogen is determined in the distillate.

Mixtures of volatile substances can often be separated by fractional distillation. This method is of great importance in organic analysis. In gas analysis use is often made of fractional condensation at lower temperatures.

Sublimation.

If a solid can be volatilized at relatively low temperatures, sublimation may be used as a means of separation. The sublimation method is rarely applied in quantitative inorganic analysis (separation of silver chloride and mercurous chloride by volatilization of the latter, volatilization of ferric chloride in a current of hydrogen chloride); it is of greater importance in organic analysis.

Use of different solvents. Extraction of solid mixtures.

Sometimes use is made of a difference in solubility of various salts in different solvents. A well-known method for the separation of the alkaline earths is based on the solubility of anhydrous calcium nitrate and the insolubility of strontium and barium nitrates in absolute alcohol. After extraction with alcohol the residue is transformed into the chlorides by repeated evaporation with hydrochloric acid. Strontium chloride is then extracted with absolute alcohol, and the barium chloride remains behind.

Lithium chloride is soluble in certain organic solvents, whereas potassium and sodium chlorides are not. Therefore quantitative separations of lithium chloride from the other alkali chlorides are based upon the extraction of the mixture of the solid chlorides with amyl alcohol, butyl alcohol, pyridine, or a mixture of ether and ethyl alcohol. If possible, it is preferable to dissolve the mixture of the chlorides in a minimum amount of water and *precipitate* with a large excess of the organic solvent. A correction for the slight solubility of sodium and potassium chlorides is applied in accurate work. It is sometimes possible to apply the extraction method with water or other solvents after a chemical or thermal decomposition of part or all the constituents.

It has been shown by Caley and Burford[1] that various substances insoluble in ordinary mineral acids and in aqua regia are soluble in concentrated hydriodic acid, either at room temperature or at the boiling point. The commercial acid with a specific gravity of 1.70 and stabilized by the addition of about 1 per cent hypophosphorous acid is suitable in most cases. If the stabilizer should interfere in later determinations, the pure acid is used.

Silica in the form of quartz, chromic oxide, and crystallized alumina in the form of alundum or that prepared by ignition at 1000° C. for a number of hours do not suffer a detectable loss on heating with constant-boiling hydriodic acid at temperatures between that of the water bath and the boiling point of the acid for periods ranging from 0.5 to 7 hours. It is possible to separate strontium and calcium sulfates from silica by treatment with the acid just below the boiling point:

$$MSO_4 + 10\ HI \rightarrow MI_2 + 4\ I_2 + 4\ H_2O + H_2S.$$

In a similar way anhydrous chromic chloride can be separated from silica:

$$CrCl_3 + 3\ HI \rightarrow CrI_3\ (\text{hydrated}) + 3\ HCl.$$

Lead sulfate and silver chloride are separated by treatment with the acid at room temperature:

$$PbSO_4 + 3\ HI \rightarrow HPbI_3 + H_2SO_4;$$
$$3\ AgCl + 4\ HI \rightarrow HAg_3I_4 + 3\ HCl.$$

Mercuric sulfide obtained by precipitation with hydrogen sulfide is usually contaminated by sulfur. The former is soluble in the constant-boiling acid and thus can be separated from the sulfur:[2]

$$HgS + 4\ HI \rightarrow H_2HgI_4 + H_2S.$$

Extraction from solution. Distribution or partition method.

Sometimes the separation of two substances in a mixture by extraction is possible if one of the compounds is soluble and the other insoluble in a second solvent which is immiscible with the first. One of the dissolved substances is soluble in both solvents and distributes itself between the two. If its solubility in one solvent is C_1 and in the other C_2 and the solute is present in the same molecular state in both solvents, it divides itself between the two solvents according to the distribution law:

---

[1] E. R. Caley and M. G. Burford, Ind. Eng. Chem., Anal. Ed. *8*, 63 (1936).

[2] *Ibid.*, 43 (1936).

$$\frac{C_1}{C_2} = K$$

in which K is the distribution coefficient or constant. Therefore, when distribution equilibrium is established, the ratio of the concentrations of the substance in each layer is equal to the constant K.

It is a matter of practical importance to estimate the number of extractions necessary to remove a substance from a solution quantitatively. The distribution coefficient of iodine between water and carbon tetrachloride is equal to $\frac{1}{85}$ at room temperature; this means that when equilibrium has been attained the iodine concentration in the carbon tetrachloride layer is 85 times greater than in the water. Suppose now that we shake 100 ml. of water containing 0.2 g. of iodine with 50 ml. of carbon tetrachloride. If x_1 g. of iodine is left in 100 ml. of water, $\frac{x_1}{100}$ g. of iodine is present per ml. The concentration in the carbon tetrachloride layer then is $\frac{0.2 - x_1}{50}$ g./ml.

$$\frac{x_1}{100} : \frac{0.2 - x_1}{50} = \frac{1}{85}$$

$$x_1 = 0.0046 \text{ g.}$$

Therefore 4.6 mg. are left in the water layer, or about 98 per cent is removed. If the carbon tetrachloride layer is separated and the aqueous solution is again shaken with 50 ml. carbon tetrachloride, about 98 per cent of the iodine left after the first distribution will be removed. If x_2 is the amount left after the second treatment, we have

$$\frac{x_2}{100} : \frac{0.0046 - x_2}{50} = \frac{1}{85}$$

$$x_2 = 0.000106 \text{ g.}$$

Therefore after the second extraction the iodine is quantitatively removed from the water layer.

We may formulate the process in general terms and determine how much of a substance is left after n extractions. Let W ml. of aqueous solution originally containing a grams of substance be extracted n times with L ml. portions of the nonmiscible solvent. The distribution coefficient $\frac{C_{\text{water}}}{C_{\text{liquid}}} = K$. The amount left after the first extraction is x_1, and therefore the amount extracted is $a - x_1$.

There will be left $\frac{x_1}{W}$ g. per ml. of aqueous solution, and the extracting liquid will contain $\frac{a - x_1}{L}$ g. per ml.

$$\frac{x_1}{W} : \frac{a - x_1}{L} = K$$

and

$$x_1 = \frac{KW}{L + KW} a.$$

It is easily seen that after the second extraction the amount x_2 left in the aqueous phase will be:

$$x_2 = \frac{KW}{L + KW} x_1 = \left\{ \frac{KW}{(L + KW)} \right\}^2 a,$$

and after n extractions the amount x_n left in the water phase will be:

$$x_n = \left\{ \frac{KW}{(L + KW)} \right\}^n a.$$

From the above it is evident that it is much better to extract several times with small portions of a liquid than to extract only once with a volume of liquid equal to the sum of the small portions. If the substance extracted divides itself favorably, the extractions are usually made in a separatory funnel. If the distribution coefficient is less favorable, the extractions are made in some form of continuous-extraction apparatus. Such devices (Soxhlet extractors) enjoy great popularity in organic chemistry.

As an example of the extraction method, Rothe's[1] separation of ferric iron in hydrochloric acid solution from smaller amounts of various other elements by shaking out the ferric chloride with ether may be mentioned. The most favorable concentration of hydrochloric acid is 6 N; if the concentration is much above or below this strength, the extraction is less complete. Two to three extractions suffice to remove practically all the iron, although according to W. F. Hillebrand and G. E. F. Lundell[2] it is never strictly quantitative, from 1 to 2 mg. remaining unextracted in the usual treatment. Moreover, according to the latter authors, there is danger that substances such as nickel or copper may be taken up by the ether to a slight extent if their concentrations are high.

---

[1] J. W. Rothe, Mitt. könig,tech. Ver. *10*, 132 (1892).

[2] W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*, p. 106

The behavior of some chlorides in the ether extraction method as summarized by Hillebrand and Lundell is presented in the following table. The values are only approximate.

TABLE XVI. EXTRACTION OF METAL CHLORIDES WITH ETHER FROM 6 *N* HCl

ELEMENT	EXTRACTED IN %	ELEMENT	EXTRACTED IN %
$Sb(SbCl_3)$	6	$Mo(MoO_3)$	80–90
$Sb(SbCl_5)$	81	$Tl(TlCl_3)$	90–95
$As(AsCl_3)$	68	$Sn(SnCl_4)$	17
$As(AsCl_5)$	2–4	$Sn(SnCl_2)$	15–30
Cu	0.05	$V(V_2O_5)$	Trace
$Au(AuCl_3)$	95	$V(V_2O_4)$	Trace
$Fe(FeCl_3)$	99	Zn	0.2
$Hg(HgCl_2)$	0.2		

The following are not extracted appreciably: Al, Bi, Ca, Cd, Cr, Co, Fe^{II}, Pb, Mn, Ni, Os, Pd, rare earths, Ag, Ti, W, U, Zr.

Dodson, Forney, and Swift[1] found that isopropyl ether offers advantages over ethyl ether for the extraction of iron from aqueous hydrochloric acid solutions, since it gives a more efficient extraction over a wider range of acid concentrations than does ethyl ether. With isopropyl ether the efficiency of extraction reaches 99 per cent at an initial acid concentration of 6.5 *N* and does not fall off appreciably until an acid concentration of 8.5 *N* is reached. Under optimum conditions (7.75–8.0 *N* HCl) the extraction is 99.9 per cent complete when 250 mg. of iron are present. With decreasing iron content the efficiency decreases; still the above authors obtained a quantitative extraction of 1 mg. of iron after shaking with three successive portions of isopropyl ether. A very satisfactory separation of iron from copper, cobalt, manganese, nickel, aluminum, chromium, zinc, quadrivalent vanadium, titanium, and sulfate can be obtained. Large amounts of quinquevalent vanadium are extracted, and phosphoric acid and molybdenum (Mo^{VI}) pass into the ether layer with ferric iron.

Separation by preferential adsorption.

In recent years much use has been made in organic chemistry of a selective adsorption of different constituents from a solution when the latter is passed through an adsorbent in columnar form. This specialized type of adsorption is called *chromatography*.[2] In quantitative inorganic analysis chromatography has found hardly any use, although application may be made of it in special cases.[1]

---

[1] R. W. Dodson, G. J. Forney, and E. H. Swift, J. Am. Chem. Soc. *58*, 2573 (1936).

[2] See L. Zechmeister and L. Cholnoky, *Principles and Practice of Chromatography* (translated from the second German edition by A. L. Bacharach and F. A. Robin-

Separation by electrolysis.

See chapter on "Electroanalysis" (p. 140).

---

son), John Wiley & Sons, New York, 1941; H. A. Strain, *Chromatographic Adsorption Analysis*, Interscience Publishers, Inc., New York, 1942.

[1] See G. M. Schwab, Angew. Chem. *52*, 666 (1939), *53*, 39 (1940); H. Erlenmeyer and J. Schmidlin, Helv. Chim. Acta *24*, 878, 1213 (1941).

CHAPTER VII

THE FORMATION AND PROPERTIES OF PRECIPITATES

Colloidal solutions.

In gravimetric analysis we are usually dealing with slightly soluble substances which behave like strong electrolytes. The saturated solutions of most precipitates in water do not contain the salts as such but in the form of their electrolytic dissociation products, in other words, as ions. These ions are extremely small, their sizes being of the order of a few Ångström units (Å. = 10^{-8} cm.),[1] and of the same order of magnitude as those of the molecules of the solvent. Such true solutions, as well as other (molecular) solutions, are optically "empty." By this we mean that if part of the solution is illuminated by a powerful beam of light, no scattering of the light is observed when the solution is viewed at right angles to the incident light (Tyndall effect). If particles having a size larger than about 100 Å. are suspended in the solvent, a distinct Tyndall effect will be observed. A true solution is perfectly clear under the ultramicroscope, and no particles can be observed. If particles with a size larger than 10 mμ are present in the solution, they will scatter light and will thus become visible in the ultramicroscope. Under the ultramicroscope we do not see the particles themselves but their diffraction images. With an ordinary microscope the limit of resolvability is of the order of 0.25 μ only.

The fact that a solution appears clear when examined with the naked eye or even with the ordinary microscope is therefore no proof that the state of subdivision of the dissolved substance is of the molecular order. This can be easily demonstrated by passing a current of hydrogen sulfide gas through a solution of arsenious oxide. The resulting liquid has an orange color and appears clear if examined with the naked eye or with the microscope. With the ultramicroscope, however, the picture is entirely different; myriads of bright particles in rapid, random motion are observed. Also if the liquid is placed in a strong beam of light, a marked scattering is noticed.

Our orange "solution" of arsenious sulfide has properties which are entirely different from those of "true" solutions. It will be recalled that arsenious sulfide is very slightly soluble in water, much less so than barium sulfate for example. Nevertheless, we can prepare "solutions" containing more than 10 g. of As_2S_3 per liter. The solute in this solution is not present in the molecular or ionic state, but in the form of aggregates, each of which contains many molecules. In distinction from true molecular solutions, a solution of this type is called a *colloidal* solution. The colloidal state is characterized by particles whose size varies between 100 and 1 mμ. Colloidal solutions have this in common with molecular solutions, that as a rule they can be filtered unchanged through quantitative filter paper. The pores of ordinary filter paper are large enough to let the colloidal particles pass through. However, if filters with extremely small pores are used, the so-called *ultra-filters* (made of collodion or parchment), molecular solutions will pass unchanged, whereas colloidal particles are retained. The osmotic properties of molecular solutions (osmotic pressure, freezing-point lowering, and boiling-point elevation) are relatively simple functions of the molecular concentration. In a colloidal solution, however, the finely divided particles have hardly any influence upon the osmotic properties of the solvent. Since the colloidal particles do not pass a collodion or parchment membrane, they can thus be separated from electrolytes by the process of *dialysis*.

---

[1] *Units and dimensions:* 1 μ = 10^{-3} mm.; 1 mμ = 10^{-6} mm.; 1 Ångström unit = 1 Å. = 10^{-7} mm. = 0.1 mμ.

We may distinguish between two types of colloidal solutions:

1. ***Suspensoids, or hydrophobic (lyophobic) colloids.*** The particles of these show no, or only a slight, attraction for water, as the name indicates. The solutions are only slightly viscous; if flocculated by the addition of a suitable electrolyte, the particles settle down in a filterable form. Such solutions are often called *sols*. Under suitable conditions, sols of most slightly soluble inorganic compounds may be prepared (metal sulfides, ammonium phosphomolybdate, silver iodide, etc.).

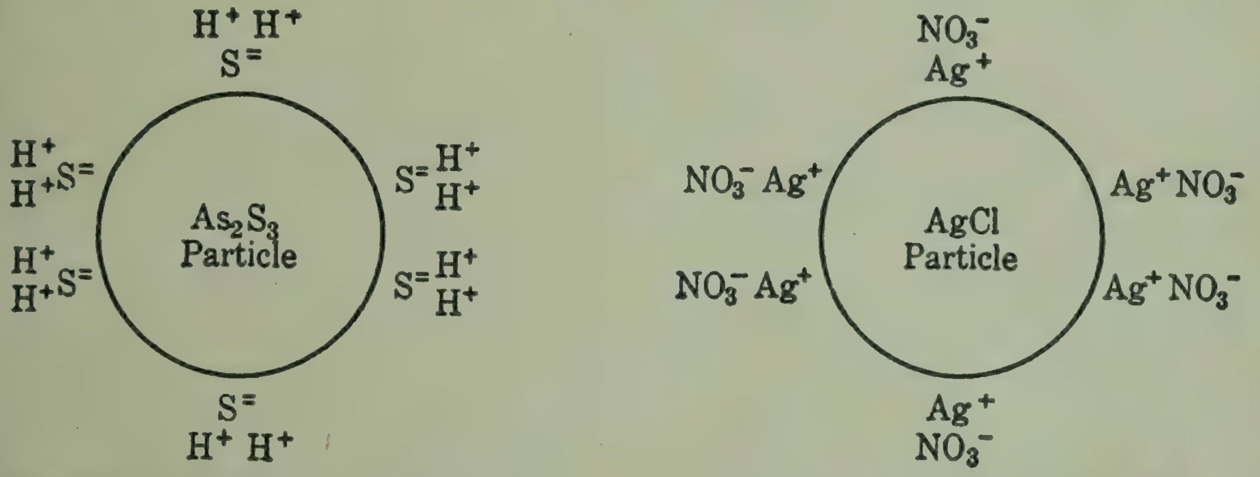
2. ***Emulsoids, or hydrophylic colloids.*** The particles of these have a strong affinity for water, and the colloidal solutions are highly viscous. Relatively large amounts of electrolytes are necessary to cause precipitation; the flocculate keeps water strongly adsorbed and has a tendency to form jelly-like masses. Many of the organic compounds which are of great practical importance, such as the proteins and higher carbohydrates, can form gels. A few of the inorganic precipitates are usually obtained in the hydrophylic form; for example, silicic acid and hydrous aluminum and stannic oxides. On addition of acid to a dilute sodium silicate solution, the latter remains perfectly clear. The silicic acid formed is in colloidal solution in a finely divided and highly hydrated state. On evaporation to dryness, it separates but not in an entirely insoluble form. If the residue is treated with water, a small part of the silica goes into colloidal solution again. Evaporation with hydrochloric or perchloric acid is necessary to transform the silicic acid to a less hydrated and also less "soluble" state. Some gelatinous precipitates have properties intermediate between those of suspensoids and emulsoids.

Gels are very hygroscopic, and it is hard to remove all the adsorbed water, even on ignition. This case is met with in the determination of aluminum by precipitation as the hydrous oxide. The precipitate is ignited at a high temperature and must be heated a long time before all water is removed. The ignited residue is still hygroscopic.

From the analytical viewpoint sols are very important, and for this reason some of their properties will be discussed. In the first place the formation of colloidal solutions must be avoided because the particles pass through ordinary filters. Colloidal solutions must also be avoided as far as possible because the flocculated particles have an enormous surface development and correspondingly great adsorptive powers. In a later chapter the adsorptive properties of precipitates will be dealt with in detail. It may simply be mentioned here that foreign constituents of the solution may be adsorbed at the surface of the flocculated particles and thus contaminate the precipitate.

Stability of sols. Flocculation. Peptization.

Finely divided particles of a slightly soluble substance can be kept in colloidal solution if they are given an opportunity to acquire an electric charge. This is accomplished by the adsorption of anions or cations on the surface of the particles; in the former case they will have a negative charge and in the latter case a positive charge. Every precipitate has a tendency to adsorb its own ions. For example, it has been shown experimentally that metal sulfides have strong adsorptive properties towards sulfide ions, and silver halides for silver ions and halide ions, respectively. It should be realized that if adsorption of the sulfide ion by a metal sulfide occurs, an equivalent adsorption of some cation present in the solution must also take place, for otherwise electroneutrality of the solution would not be maintained. In the preparation of colloidal sulfide solutions the sulfide is usually adsorbed in the form of hydrogen sulfide, if the latter is in excess in the solution. Sulfide ions are primarily adsorbed, and they are attracted so strongly that they are fixed on the surface of the particles. The other ions, which may be called the *counter ions* (in this particular case hydrogen ions), cannot approach the surface so closely and will stay at a very small distance, although in the immediate neighborhood of the surface, since the electrostatic forces between the negative ions on the surface and the positive counter ions are very large. According to this picture a so-called *electrical double layer* is set up between the particles and the solution (see Fig. 5). A colloidal particle of arsenious sulfide has a negatively charged surface, whereas the surrounding liquid is positive with respect to the particle. If an electric current is passed



Colloidal particle of As_2S_3 with negative charge. $S^=$ is inner or stabilizing ion (fixed on surface). H^+ is counter ion.

Colloidal particle of AgCl with positive charge. Ag^+ is inner or stabilizing ion (fixed on surface). NO_3^- is counter ion.

Fig. 5

through the solution, the negative particles will move towards the anode, just as anions do, although the mobility of the colloidal particles is much smaller than that of ions. The existence of the electrical double layer is responsible for the stability of the colloid. All the particles have a charge of the same sign, and upon close approach they will not collide but will repel each other. With the ultramicroscope a rapid Brownian movement is observed. If by some means the electrical double layer is destroyed, the sol is no longer stable and the particles will flocculate. This destruction of the double layer can be accomplished by the addition of a sufficient amount of electrolyte. The minimum amount of electrolyte necessary to flocculate the colloid is called the *flocculation value.* The latter depends primarily upon the kind of charge (+ or −) of the colloidal particles and the valence, and more or less upon the specific properties of the ions of opposite charge of the flocculating electrolyte. In experiments with arsenious sulfide, for example, Linder and Picton[1] found that the ratios of the "flocculation" values of electrolytes containing uni-, di-, and trivalent cations were of the order of 500 : 10 : 1. If on the other hand we are dealing with a positively charged colloid, the flocculation value depends primarily on the valence of the anion.

Some illustrative data are given in the following tables. The individual nature of the flocculating ion has some influence as well. This holds especially for organic aromatic ions, the flocculation values of which as a rule are much smaller than those of inorganic ions of the same valence.

The ions which determined the original charge of the particles will remain on the surface during, and more or less after, the flocculation. This process involves an equivalent adsorption of the counter ions by the flocculated precipitate. Experimentally it has been proved that strongly flocculating ions replaced the originally adsorbed counter ions at the surface of the particles. If, for example, an arsenious or mercuric sulfide sol is flocculated with barium chloride, the precipitate will contain

TABLE XVII. FLOCCULATION OF NEGATIVE ARSENIC TRISULFIDE SOL[2]

Milliequivalents of various salts required for flocculation

ELECTROLYTE	FLOCCULATION VALUE	ELECTROLYTE	FLOCCULATION VALUE	ELECTROLYTE	FLOCCULATION VALUE
(univalent cations)		(divalent cations)		(trivalent cations)	
KCl	98	$CaCl_2$	1.31	$FeCl_3$	0.136
NaCl	103	$SrCl_2$	1.23	$AlCl_3$	0.062
NH_4Cl	63	$BaCl_2$	1.18	$Al_2(SO_4)_3$	0.074
HCl	59	$MgCl_2$	1.14	$La_2(SO_4)_3$	0.074
KNO_3	105	$NiCl_2$	1.52	$Ce_2(SO_4)_3$	0.074
KBr	101	$MgSO_4$	2.10		
KI	102				
K_2SO_4	123				

---

[1] S. E. Linder and H. Picton, J. Chem. Soc. *67*, 63 (1895).

[2] *Ibid.*

Table XVIII. Flocculation of Positive Hydrous Ferric Oxide Sol[1]

Milliequivalents of various salts required for flocculation

Electrolyte	Flocculation Value	Electrolyte	Flocculation Value
$Fe(CN)_6^{----}$	0.067	BrO_3^-	31.3
$Fe(CN)_6^{---}$	0.096	CNS^-	46.9
$SO_4^{=}$	0.219	Cl^-	103
$CrO_4^{=}$	0.325	NO_3^-	131
$C_2O_4^{=}$	0.238	I^-	154

an adsorbed layer of barium sulfide or, if we use lanthanum chloride, of lanthanum sulfide. On the other hand, if the flocculation is carried out with an electrolyte, the cation of which is only slightly adsorbable, for example with potassium or sodium chloride, the replacement is incomplete, and the precipitate will contain both adsorbed hydrogen and potassium sulfide. From the above it is evident that a flocculated colloid is always contaminated by surface adsorption. Part of the adsorbed electrolyte can be removed by thorough washing with water. In the washing one is often confronted with another difficulty. During the washing process the electrolyte concentration in the supernatant liquid will become smaller than the flocculation value, with the result that the particles may go into colloidal solution again. This phenomenon is called *peptization* and has to be considered in analytical procedures. In the precipitation of silver with an excess of halide or of phosphate as ammonium phosphomolybdate or of nickel as nickel sulfide, one often encounters the difficulty that on washing, the precipitate "runs through the filter." This peptization can be prevented by washing with a suitable electrolyte solution which does not interfere in the subsequent steps of the determination. Silver halides can be washed with a dilute solution of a strong acid, and the phosphomolybdate or nickel sulfide with a solution of an ammonium salt. When the washed precipitate is ignited, the adsorbed electrolyte is removed by volatilization. If the flocculated colloid has a positive charge, as is the case in the precipitation of halides with an excess of silver, it is harder to make the adsorbed electrolyte harmless.

A fortunate circumstance, however, is that flocculated colloids usually undergo a rapid aging, especially on digestion, which decreases their total surface and the amount of adsorbed electrolyte. This aging of precipitates is discussed in a later section.

An understanding of the simple properties of colloidal solutions is therefore of great value in the analytical laboratory. Sometimes one is faced with the difficulty that a precipitate shows a pronounced tendency to remain in colloidal solution. This for example occurs in the precipitation of lead with an excess of chromate. Part of the lead chromate is peptized by the excess of chromate and has a negative charge. Addition of a trace of a trivalent cation, such as aluminum in the form of its chloride, is very effective in obtaining complete flocculation and an easily filterable precipitate (the adsorbed aluminum does not interfere in the volumetric lead determination). In other cases one must beware of the adsorptive properties of the precipitate formed. Hydrous oxides precipitated from weakly acid medium are positively charged. The hydroxyl ions in the solid oxide have a great affinity for hydrogen ions and consequently tend to adsorb an equivalent amount of anions with the hydrogen ions. The higher the valence of the anion the stronger it will be adsorbed. If, for example, hydrous ferric oxide is quantitatively precipitated at a pH of 4 to 5 and the solution contains sulfate, a great deal of the latter will be adsorbed, and it will not be removed by washing. If on the other hand the precipitation is carried out from ammoniacal medium, a primary adsorption of hydroxyl ions takes place, and the precipitate acquires a negative charge. It will no longer adsorb other anions but exerts a strong adsorptive effect on cations. Again the adsorbability of the latter increases with increasing valence. By precipitation of hydrous oxides from ammoniacal medium, there is always an adsorption of smaller or larger amounts of calcium, magnesium, nickel, copper, etc., when these are present in the solution. These cations cannot be removed by washing, and even a reprecipitation of the oxide is often not effective in affording a quantitative separation. If possible, therefore, one should endeavor to separate hydrous oxides from anions by precipitation in alkaline medium, and from cations in acid medium.

---

[1] H. B. Weiser and E. B. Middleton, J. Phys. Chem. *24*, 30, 630 (1920).

In certain cases the adsorptive properties of colloidal precipitates may advantageously be used for the removal of interfering ions from solutions. For example, hydrous stannic oxide in very dilute nitric acid has strong adsorptive properties for phosphoric and arsenic acids. The latter can be quantitatively removed with the aid of this adsorbent. Manganese dioxide, precipitated from weakly acid medium by addition of permanganate to a solution which contains a manganous salt, carries down quantitatively antimony, tin, and bismuth.[1] Other constituents such as copper, arsenic, and others are also coprecipitated but not quantitatively.

In other cases, traces of ions present in large volumes of solvent, in too small a concentration to allow direct determination, may be accumulated on the surface of an adsorbent. Suppose that a water sample contains 1 mg. of lead per liter. If this element must be determined with a fairly high degree of accuracy, one could evaporate 10 liters or so of water and determine the lead in the residue. The same result, however, can be obtained in a much simpler way by shaking a large volume of the water with a little calcium carbonate. The latter adsorbs all the lead; the adsorbent is collected by filtration or centrifugalization and, without washing, is dissolved in dilute acetic acid, after which the lead is precipitated as chromate.

Summarizing the facts important in analytical chemistry, we find:

1. That peptization of colloidal precipitates can be prevented by addition of, and washing with, a suitable electrolyte.

---

[1] H. Blumenthal, Z. anal. Chem. *74*, 33 (1928); S. Kallmann and F. Pristera, Ind. Eng. Chem., Anal. Ed. *13*, 8 (1941).

2. That colloidal precipitates contain impurities in the adsorbed state. By proper washing with dilute acid or ammonium salt solutions, it is often possible to replace the adsorbed electrolyte with a compound which is volatile at higher temperatures.

3. That in many cases slimy precipitates can be obtained in an easily filterable form by the addition of a trace of gelatin (see p. 109).

4. That use can be made of the adsorptive properties of finely divided precipitates in removing certain ions from solution or for concentrating traces of ions prior to their determination.

The formation and particle size of precipitates.

The particle size and form of a precipitate depends upon the conditions under which it has been formed, the individual characteristics of the particular substance, and the treatment before filtration. Most of the ordinary precipitates, even those of colloidal dimensions, separate in a crystalline state.[1]

Among the factors which determine the particle size of the precipitate formed, there is one of predominant importance, namely, the *relative supersaturation* of the solution with respect to the slightly soluble substance. This concept was introduced by P. P. von Weimarn [2] and can be formulated by the expression:

$$\frac{Q - S}{S}$$

where Q is the total concentration of the substance that is to precipitate and S is the solubility of coarse crystals of the substance. $Q - S$ denotes the supersaturation at the moment precipitation begins. The above expression is not exact because the solubility, S, is a function of the size of the particles. The primary particles have a greater solubility than those of larger size ($> 1\ \mu$), as discussed in the next section. In addition, the value of S depends upon the excess of the common ion and the total electrolyte concentration, and as a rule it is not exactly known under specified experimental conditions. Still, by changing $\frac{Q - S}{S}$ for a given precipitate, it is possible to change the size of the particles between wide limits. In a supersaturated solution, nuclei of the substance are formed which will grow to larger dimensions. The speed of formation of these nuclei is a function of the degree of supersaturation and probably of the concentration of the reacting components. If this degree of supersaturation is small, relatively few nuclei are formed, and these will grow slowly at the cost of the dissolved material. Under these conditions fairly large and perfect crystals may be expected. The number of nuclei formed increases with increasing supersaturation, and therefore the number of particles separating at the very start (primary particles) will also be increased. In the most extreme case all the material present is precipitated in the form of primary particles which cannot grow at the cost of the dissolved material, since the solution is no longer supersaturated. The size of such a primary precipitate can change by secondary processes only (see the section on "aging of freshly prepared precipitates").

---

[1] A body is said to be crystalline when the molecules, atoms, or ions that make it up are regularly arranged in a lattice as revealed by X-ray examination.

[2] P. P. von Weimarn, *Zur Lehre von den Zuständen der Materie*, Bd. 1, Text; Bd. II (1913); *Die Allgemeinheit des kolloiden Zustandes*, Th. Steinkopff, Dresden, 1925.

The rate of growth V of the primary particles to larger crystals is given by the Noyes-Nernst expression:

$$V = \frac{D}{l} A(Q - S)$$

in which D is the diffusion coefficient of the crystallizing compound, l the length of the diffusion path, and A the surface area of the disperse phase. At a given temperature and rate of stirring this equation can be written as follows:

$$V = k(Q - S).$$

From the above, it is evident that in general the particle size of a precipitate decreases with increasing concentration of the reacting components. As a demonstration some experiments of von Weimarn (*loc. cit.*) with barium sulfate are tabulated below.

TABLE XIX. SEPARATION OF BARIUM SULFATE FROM SOLUTIONS AT VARIOUS DEGREES OF SUPERSATURATION

Concentration of sulfate and of barium respectively 3 N to 7 N: A gelatinous precipitate is formed; practically all the water in the solution is adsorbed. The containing vessel can be inverted without the contents running out. The gel is far from being stable; the growth of large particles at the expense of small ones is fairly rapid. The primary precipitate is so fine that the particles are not resolvable by either the microscope or the ultramicroscope.

Concentration of reacting components 0.75 N to 3 N: The primary precipitate is curdy and of colloidal dimensions. The particles appear as points at a magnification of 1500 ×.

Concentration of 0.05 N: The primary precipitate consists of feathery and star-shaped crystal skeletons.

Concentration of 0.005 N: The precipitate consists of compact crystal skeletons.

Concentration of *ca.* 0.001 N: The mixture remains clear for about five minutes and then becomes opalescent. Precipitation continues for two hours. After that time the crystals have a size of about 5 μ.

Concentration of *ca.* 0.0002 N: The precipitate appears after about a month has elapsed. At the end of six months the length of the largest crystals is about 30 μ and their breadth 15 μ.

It was stated above that most precipitates, even those of colloidal dimensions, have a crystalline structure. In some cases, however, *amorphous* precipitates which do not show the X-ray pattern of a crystalline substance may be formed. In order to understand this, we may, with Haber,[1] consider two factors which determined the nature of the primary precipitate, namely, the *aggregation velocity* and the *orientation velocity.* If the solubility limit is exceeded, the molecules, or aggregates of molecules, will have a tendency to unite and thus form larger aggregates. This aggregation velocity is a function of the degree of supersaturation; the larger the latter, the less regular the separated aggregates will be. Besides the supersaturation, the absolute concentration of the reacting ions will also be of significance. The primary aggregates formed, in which the molecules are arranged in a more or less chaotic manner, are not stable. By loss of energy they tend to reach a state of equilibrium, in which the molecules become regularly arranged in a crystal lattice. The speed with which this process takes place is called the orientation velocity. It is evident then that the form in which a precipitate separates depends upon the competition between the aggregation and orientation velocities. If the supersaturation is extremely large, the aggregation velocity may dominate, and the separated particles will not show an X-ray pattern; in other words, they are *amorphous.* On standing (aging), the amorphous precipitate will transform more or less rapidly into a crystalline modification. The orientation velocity is different for different substances. Strongly polar salts such as silver chloride and barium sulfate, for example, have a high orientation velocity and separate in a crystalline form.

In cases where we are dealing with substances like the hydrous oxides, the orientation velocity decreases with the number of hydroxyl ions attached to the metal ion. The hydroxides of the divalent metals magnesium, cadmium, and zinc are obtained in a crystalline form; hydrous ferric oxide, on the other hand, if precipitated from cold solutions is amorphous but is transformed on aging, especially on heating, into a crystalline product. Hydrous oxides of the tetravalent metals (thorium, etc.) are usually obtained in the amorphous form and on aging change extremely slowly into crystalline modifications.

From the above it may be inferred that the relative supersaturation alone does not determine the particle size of the precipitate formed, as von Weimarn assumes. The characteristic properties of the precipitate must be considered as well. Still it remains true that in any case the particle size of a slightly soluble substance formed by precipitation increases with decreasing supersaturation. Use is made of this fact:

(a) Precipitations are usually carried out in hot solutions, since the solubility of the precipitates is generally greater at high temperatures than at room temperature.

(b) Large crystals can be obtained by precipitation from extremely dilute solutions, especially at high temperatures, by proceeding in the following way: Some water or dilute acid is placed in a beaker. From one buret one slowly delivers, with efficient stirring, a measured volume of the solution to be analyzed and simultaneously from another buret a solution of the reagent. The speed of addition of both solutions is regulated in such a way that there is never a large excess of either the ion to be precipitated or of the precipitant, until the precipitation is complete. Coarse crystals of substances which usually precipitate in a finely divided state (e.g., barium sulfate) may be obtained in this way.

---

[1] F. Haber, Ber. *55*, 1717 (1922).

(c) The solubility of the precipitate is increased by the addition of a suitable reagent. After the precipitate has been formed, the effect of the solvent upon the solubility is neutralized in some suitable way. In order to obtain relatively large crystals of calcium oxalate, the latter may be precipitated from dilute acid medium; after the formation of the precipitate, the acid is neutralized with ammonia to precipitate the last traces. Willard [1] succeeded in obtaining very large crystals of calcium oxalate by adding enough hydrochloric acid to the calcium oxalate mixture to prevent precipitation. An excess of urea was added to the solution, which was then heated. The urea is slowly hydrolyzed:

$$CO(NH_2)_2 + H_2O \rightarrow CO_2 + 2\,NH_3$$

and the ammonia formed neutralizes the acid. Under these conditions the speed of formation of calcium oxalate is extremely low, and large crystals result.

Silver chloride is usually obtained in the form of a flocculated colloid. However, if it is dissolved in ammonia and the latter removed by slow volatilization, fairly large crystals of silver chloride will separate.

Solubility and particle size.

For many years it has been known that the solubility of very small crystals is greater than that of crystals of large dimensions, owing to the greater surface energy of the former. When the crystal size becomes smaller than 1 to 2 μ, the solubility quite generally increases with increasing surface development.[2] Surface tension tends to decrease the exposed surface, and therefore a fine powder exhibits a tendency to acquire a smaller surface, the process being accomplished by the small-sized particles dissolving and crystallizing again on the surface of larger particles or by the cementing together of particles.

G. A. Hulett [3] has experimentally proved that there exists a difference in solubility between coarse and fine particles of gypsum ($CaSO_4 \cdot 2\,H_2O$) and of barium sulfate. More extensive investigations have been carried out by M. L. Dundon and E. Mack.[4] Dundon's results give the order of surface tension of various crystals, and it is possible to calculate from them the solubility of the substances at various particle sizes (Table XX).

---

[1] H. H. Willard and N. H. Furman, *Elementary Quantitative Analysis*.

[2] For a literature review compare H. Freundlich, *Kapillarchemie*, 2d ed. (1922); Akadem. Verlagsgesellschaft, Leipzig, pp. 207–211; R. A. Gortner, *Outlines of Biochemistry*, p. 150, John Wiley and Sons, New York, 1929; T. B. Smith, *Analytical Processes*, pp. 239–278 (1929).

[3] G. A. Hulett, Z. physik. Chem. *37*, 385 (1901); *47*, 357 (1909).

[4] M. L. Dundon and E. Mack, J. Am. Chem. Soc. *45*, 2479 (1923); Dundon, *ibid.* *45*, 2658 (1923).

TABLE XX. SURFACE TENSION OF SOME SUBSTANCES ACCORDING TO M. L. DUNDON

SUBSTANCE	M *	d *	MOL. VOL.*	r IN μ *	INCREASE IN SOLUBILITY IN % *	TEMP. ° C.	σ *	HARDNESS (Mohs)
PbI_2	461	6.16	74.8	0.4	2	30	130	very soft
$CaSO_4 \cdot 2\,H_2O$	172	2.32	74.2	0.2–0.5	4.4–12	30	370	1.6–2
Ag_2CrO_4	332	5.52	60.1	0.3	10	26	575	*ca.* 2
PbF_2	245	8.24	29.7	0.3	9	25	900	*ca.* 2
$SrSO_4$	184	3.96	46.4	0.25	26	30	1400	3.0–3.5
$BaSO_4$								
(Hulett)	233	4.5	52	0.1	80	25	1250	2.5–3.5
(Dundon)				0.2	90	30	3000	2.5–3.5
CaF_2	78	3.18	24.6	0.3	18	30	2500	4

* M denotes the molecular weight; d, the density of crystal; Mol. Vol., the molecular volume; r, the radius of particle expressed in microns (microscopically measured); σ, the surface tension of particle; and "Increase in Solubility in %," the percentum increase of solubility with respect to massive crystals.

Thermodynamically it has been shown that for slightly soluble salts the following relation exists between surface tension on the one hand and solubility on the other:

$$\frac{RT}{M} \ln \frac{S_r}{S} = \frac{2\,\sigma}{dr},$$

where R is the gas constant; T, the absolute temperature; M, the molecular weight; S_r, the solubility of particles with a radius r; S, the same of macrocrystals; σ, the surface tension; and d, the density.

By means of this equation and Dundon's data, the ratio of S_r/S for barium sulfate, silver chromate, and lead iodide at a size of 0.04 μ ($r = 0.02\ \mu$), can be calculated:

	$\frac{S_{0.02}}{S}$
$BaSO_4$	930
Ag_2CrO_4	4.0
PbI_2	1.38

Whereas at this small size the solubility of barium sulfate is about 1000 times greater than that of the large crystals, the solubility of silver chromate under the same conditions has increased only 4 times and that of lead iodide only 1.4 times.

These differences explain why substances of about the same solubility, precipitated under analogous conditions, may separate with entirely different particle sizes.[1] Silver chloride and barium sulfate have a solubility product of the same order of magnitude; in spite of this, silver chloride is always precipitated as a flocculated colloid and barium sulfate in the form of microcrystals under analytical conditions. It is easy now to account for this difference. Suppose a barium solution is added to one of sulfate, and a silver solution to a chloride solution under such conditions that the "*micro supersaturation*" of barium sulfate and silver chloride is the same. The silver halides form soft crystals with low surface tension, their solubilities being more or less independent of the crystal size. In other words, the solubility of the particles first formed in the solution (nuclei) is about the same as that of larger crystals. For barium sulfate (and other alkaline earth sulfates, lead sulfate, etc.) the case is quite different. The solubility of the primary particles is much larger than that of the large crystals; therefore the solution is much less supersaturated with respect to the same particles of barium sulfate than the silver chloride solution is with respect to silver chloride. The velocity of formation of nuclei and the growth of the latter to larger crystals increase with increasing supersaturation. Therefore many more nuclei are formed in the case of silver chloride than in the case of barium sulfate. By the rapid formation of so many nuclei the solution is soon exhausted of substance, and no ions are left to contribute to a growth of the small particles; silver chloride consequently precipitates as a flocculated colloid. In the case of barium sulfate fewer nuclei are formed, and these grow at the expense of the ions left in the solution; the substance finally settles out as a microcrystalline precipitate.

---

[1] Cf. I. M. Kolthoff, J. Phys. Chem. *36*, 860 (1932).

The velocity of recrystallization of finely divided precipitates is also determined by the relation between solubility and surface tension. Finely divided precipitates of barium sulfate, calcium oxalate, etc. which are formed in not too dilute solutions recrystallize on standing to give larger crystals.

Supersaturation is a relative concept; supersaturation cannot be expressed in absolute figures unless crystals of the normal solubility are present as solid body.

Finally, it may be stated that the solubility of an amorphous precipitate is not only greater than that of the crystalline modification (or modifications) of the same substance, but what is more important, the solubility will not be constant but will depend upon the state in which the amorphous form happens to be at a given moment. The amorphous form consists of aggregates which have coalesced in a more or less arbitrary way, and it is therefore not stable but undergoes continuous transformation into a more stable crystalline state. Therefore in dealing with amorphous precipitates, one must exercise caution in making calculations on the basis of the mass-action law when using solubility figures of the stable form.

Aging and filterability of precipitates.

A freshly formed precipitate may undergo changes on aging in contact with the mother liquor whereby the total surface of the primary product decreases as a rule and particles of larger size result.

1. ***The precipitate is formed from relatively concentrated solutions at room temperature.*** Under these conditions the relative supersaturation is great, and extremely fine particles will separate. This primary precipitate as a rule consists of very small crystals, which are, however, far from perfect. They have been formed so rapidly that they have a discontinu-

ous structure and consist of amicroscopic units (containing relatively few ions or molecules) which fit together like bricks in a wall. These discontinuities give rise to an *internal surface.* The total surface of such crystals is much larger than that measured microscopically. On aging, especially on digestion in contact with the mother liquor, the crystals tend to perfect themselves by a recrystallization process. Quite generally when a precipitate exists in equilibrium with its saturated solution, there is still an interaction between the solid and liquid phases. Ions continuously go into the solution and deposit on the surface again (kinetic exchange). At equilibrium, the speed with which the ions go into solution is equal to the speed with which they deposit on the surface.

When a precipitate is quickly formed under conditions of large relative supersaturation, the primary particles are very imperfect and small. Such primary particles are of colloidal dimensions and would run through filter paper even of fine pore size. That suspensions of precipitates formed under the above conditions can be filtered and made to yield clear filtrates is due to the fact that the primary particles are flocculated by the excess of electrolyte present in the solution. This flocculation gives rise to the formation of agglomerates. Depending upon the conditions, these agglomerates may contain millions of primary particles which share their water jackets. The primary particles are extremely imperfect, and lattice ions leave the "imperfect spots" of the surface very rapidly and redeposit at less active spots. This means that when the precipitate is left in contact with the mother liquor the primary particles are subject to rapid and continuous recrystallizations. Experimentally, this has been shown to be true in the aging of rapidly formed precipitates of lead sulfate,[1] barium sulfate,[2] silver chloride,[3] silver bromide,[4] and lead chromate.[5] Increase of the temperature of the supernatant liquid greatly promotes the speed of recrystallization. It is not to be expected that the rapid recrystallization of the primary particles will affect the magnitude of the external surface of the precipitate considerably. Still it is found, especially during the early stages of the aging in which the recrystallization is particularly prominent, that the external surface of the precipitate decreases markedly. Thus, for example, it was found that the size of barium sulfate particles obtained upon rapid mixing of 0.1 M barium nitrate and 0.1 M sodium sulfate decreased more than four times when the precipitate was allowed to stand in contact with the mother liquor for a day. This decrease of the surface is attributed to a *cementing together* of the primary particles in the agglomerates as a result of the continuous recrystallization. As stated above, lattice ions at highly active spots enter into the liquid film shared by the primary particles. This liquid film becomes supersaturated with regard to more normal surface where the lattice ions deposit again. However, part of the lattice material may also deposit in the liquid film between the particles, thus forming a bridge and cementing the particles together. Upon further aging, the cementing process may become more complete by the entire elimination of the liquid film by lattice material between the particles in an agglomerate, thus giving rise to the formation of large crystals with a mosaic structure.

---

[1] I. M. Kolthoff and Ch. Rosenblum, J. Am. Chem. Soc. *56*, 1264 (1934); *57*, 597, 607 (1935); Kolthoff and W. von Fischer, *ibid. 61*, 191, 195 (1939).

[2] I. M. Kolthoff and G. Noponen, J. Am. Chem. Soc. *60*, 197, 499, 505 (1938).

[3] I. M. Kolthoff and H. C. Yutzy, J. Am. Chem. Soc *59*, 916, 1634, 2029 (1937).

[4] I. M. Kolthoff and A. S. O'Brien, J. Am. Chem. Soc. *61*, 3409, 3414 (1939); J. Chem. Phys. *7*, 401 (1939); Kolthoff and F. T. Eggertsen, J. Am. Chem. Soc. *61*, 1036 (1939).

[5] I. M. Kolthoff and F. T. Eggertsen, J. Am. Chem. Soc. *62*, 2125 (1940); *63*, 1412 (1941).

The rapid recrystallization of the primary particles is of great analytical importance. The particles which have been formed rapidly from greatly supersaturated solutions are usually badly contaminated by coprecipitated foreign material from the solution. During the recrystallization, this coprecipitated material will enter the liquid film and be expelled from the particles. Thus, the recrystallization results not only in a perfection of the tiny crystals but also in a purification. The result of aging of a precipitate, especially at higher temperatures, in connection with the purity of the precipitate is discussed in the next chapter, which deals with coprecipitation.

In a precipitate of the above nature the rapid recrystallization is predominant as compared to other changes which may occur on aging. However, we may have to consider another type of aging, usually called *Ostwald ripening*, which may be of importance when the precipitate is digested at higher temperatures.

In the preceding pages it has been pointed out that particles of small dimensions have a greater solubility than particles of larger size. Therefore, on aging, especially at higher temperatures, the smaller particles tend to go into solution, and the larger particles grow at the expense of the small ones. The speed of crystallization increases with increasing solubility of the particular substance in the medium. If the solubility is extremely small, the recrystallization takes place very slowly as a rule. Thus Dundon (*loc. cit.*) boiled a suspension of barium sulfate (size $0.2\ \mu$–$0.3\ \mu$) under a reflux condenser for a week with no visible change in particle size, even when seeded with large crystals. H. M. Trimble[1] digested finely divided barium sulfate for a few hours in the presence of hydrochloric acid at 100°. Microscopic examination showed that the average size of particles (between 1 and 4 μ) remained unchanged during digestion, but still the precipitate was easily filterable. If the mixture was stirred during the digestion, no clear filtrate was obtained even after three or four days.

2. ***The precipitate separates from relatively dilute solutions at higher temperatures.*** Under these conditions the primary precipitate usually consists of particles having a size of the order of 1 μ and greater. It should be realized that the primary precipitate has been formed very quickly and has not had an opportunity to grow to perfect crystals. On digestion, therefore, a process of perfection takes place again, whereby the internal surface of the precipitate is decreased. This perfection is of great analytical significance, since as a result of the decrease in surface the amount of foreign ions primarily adsorbed will decrease. As a rule a

---

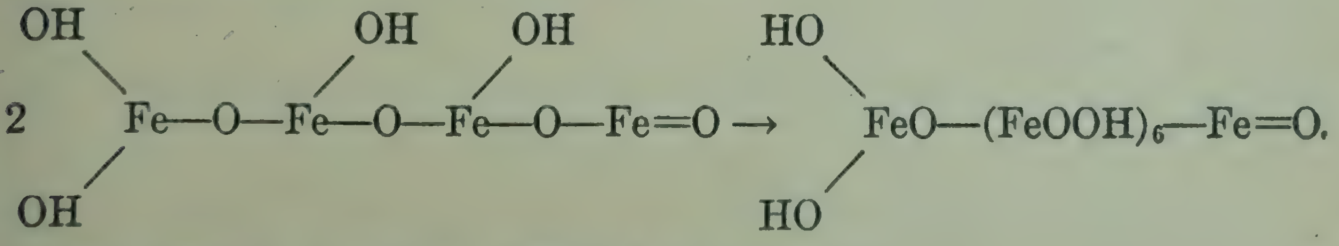
[1] H. M. Trimble, J. Phys. Chem. *31*, 601 (1927).

purer precipitate will be obtained after digestion. It is often stated that digestion of a precipitate is necessary to ensure complete precipitation. However, in many cases precipitation is complete a few minutes after addition of the excess of reagent. In the chapter dealing with coprecipitation we shall show the beneficial effect of digestion upon the purity of precipitates formed under various conditions.

A simple experiment may be described here which demonstrates the decrease of the internal surface on aging, even at room temperature. Barium sulfate shaken immediately after precipitation with a permanganate solution assumes a slightly pink color after a few minutes. The intensity of the latter, an indication of the amount of permanganate in the crystals, increases with time and approaches a maximum after a day or two. The permanganate is incorporated during the perfection (i.e., recrystallization) of the fresh precipitate. Such a precipitate is not decolorized by washing and retains its color if shaken with a solution of hydrogen peroxide or oxalic acid in 2 N hydrochloric acid. However, if the barium sulfate, after precipitation, is allowed to stand for some days before adding the permanganate, hardly any of the latter compound is taken up, thus showing that the primary precipitate has undergone a drastic perfection.

3. ***The primary precipitate consists of a metastable modification.*** In this case the primary precipitate may be transformed into a stable crystalline form on standing or on heating. This results in a rapid recrystallization of the precipitate. This case is encountered, for example, in the precipitation of calcium oxalate at room temperature from fairly concentrated solutions. The primary precipitate consists of higher hydrates, which on digestion are transformed into the stable monohydrate, with the result that a purer precipitate is usually obtained after digestion. This is readily understood when one realizes that the stable modification is formed very slowly and consists of much more perfect crystals than the primary precipitate.

4. ***The primary precipitate is amorphous (for example, hydrous ferric and aluminum oxides).*** On aging at higher temperatures these precipitates are transformed into a crystalline modification, the process being accompanied by a decrease in the total surface. Moreover, an aging as a result of a chemical interaction between the particles may occur. This happens when the primary, amorphous particles are highly reactive and are of such a nature that they react with one another in a chemical way. An example of this kind is found in the aging of hydrous ferric oxide (ortho ferric hydroxide). According to Krause,[1] in the early stages of aging two molecules of the ortho hydroxide react to form a polymerization product containing 8 atoms of iron:



$$2\ (HO)_2Fe{-}O{-}Fe(OH){-}O{-}Fe(OH){-}O{-}Fe{=}O \rightarrow (HO)_2FeO{-}(FeOOH)_6{-}Fe{=}O.$$

---

[1] See review by A. Krause, Kolloid Z. *72*, 18 (1935).

More molecules of the ortho hydroxide can be added, and finally agglomerates with a chain structure containing 40 to 50 atoms of iron are formed. Although there is a definite ordering in these agglomerates, they are not yet crystalline. The polymerization is accompanied by a dehydration and a change of color. The aging may result in the formation of yellow amorphous ferric acid with a ring structure and finally in the formation of crystalline goethite. The speed and also the kind of aging are greatly dependent upon the composition of the aging medium.

Hydrous oxides formed under ordinary analytical conditions age rather slowly, and the precipitates retain their original gelatinous character for a long time. If possible one should avoid the formation of such gelatinous precipitates in gravimetric procedures. This may sometimes be accomplished by choosing such conditions of precipitation that the supersaturation is not too great. In the precipitation of hydrous aluminum oxide, for example, one can add an excess of sodium hydroxide, with which the aluminum forms a soluble aluminate. A current of carbon dioxide is passed slowly through the warm solution, the gas neutralizing the excess of strong base. Under these conditions a heavy precipitate of aluminum oxide hydrate is formed, which settles rapidly and can be filtered easily. The procedure is rarely used on account of increased coprecipitation. Willard and Tang[1] obtained a dense precipitate of aluminum oxide hydrate by adding a succinate buffer and urea to the solution. Upon heating, the urea hydrolyzes slowly to ammonium carbonate, and consequently the pH increases slowly. The precipitation is complete in a pH region of 4.2 to 4.6. The precipitate is formed slowly under conditions of slight supersaturation and therefore is of a coarse nature.

Gelatinous precipitates are hard to filter and purify by a washing process. The primary particles are very much smaller than the pores of the filter paper, but they cannot pass through, since they are held together in the form of much larger secondary aggregates. Gelatinous precipitates have a marked tendency to clog the filter, and therefore a coarse-textured filter paper should always be used when dealing with such hydrated gels. But even then it sometimes happens that the jelly-like precipitate will form a nearly impervious layer over the surface of the filter paper. "Filtration will then entirely cease, for although the capillary interstices between the primary particles are filled with liquid, it is impossible to drive this through even with the aid of suction below or pressure above the filter, for obviously if sufficient force is used to move the water between the primary particles, it would also disintegrate the secondary aggregates and force the primary particles through the filter. Doubtless an ultra filter, the pores of which are smaller than the primary particles, could be used, but the slowness of the process would make it of little value for ordinary analytical purposes."[2] Membrane filters, made from esters of cellulose by evaporation from a suitable solvent, have been strongly recommended for the filtration of gelatinous precipitates.[3] Macerated filter paper is very useful in filtering and washing gelatinous precipitates (p. 184).

---

[1] H. H. Willard and N. K. Tang, Ind. Eng. Chem., Anal. Ed. *9*, 357 (1937).

[2] T. B. Smith, *Analytical Processes*.

[3] See R. Zsigmondy and W. Bachmann, Z. anorg. allgem. Chem. *103*, 119 (1918); R. Zsigmondy and G. Jander, Z. anal. Chem. *58*, 241 (1919); G. Jander and J. Zakowski, *Membranfilter, Cella- und Ultrareinfilter*, Akad. Verlagsges., Leipzig, 1929.

Finely dispersed precipitates can be coagulated by adding very small amounts of organic substances, which behave as lyophilic colloids, such as gelatin, agar, and gum arabic. Contrary to ordinary behavior the latter usually do not stabilize suspensoid sols if present in minute traces, but they bring about rapid and complete flocculations. This phenomenon is called *sensitization.* This sensitization is of great analytical importance, as shown by Caldwell and Moyer.[1] Especially in cases where we are dealing with finely dispersed precipitates which by their slimy character are hard to filter, the addition of a suitable sensitizer may improve the conditions considerably. Thus it was shown by Caldwell and Moyer[2] that a well-coagulated, easily filterable zinc sulfide is obtained if 0.5–2.0 mg. of gelatin are added before or after the precipitation with hydrogen sulfide from a solution containing much ammonium sulfate. Gelatin has also been recommended[3] to obtain an easily filterable precipitate of calcium fluoride. It also seems useful in obtaining filterable precipitates of hydrous oxides, like those of zirconium, titanium, ytterbium, tantalum, columbium, nickel, etc. Gelatin seems to be of special importance in the quantitative precipitation of silica, which has a strong tendency to stay in solution as a hydrophylic colloid. Interesting results in this connection were obtained by Weisz and Sieger.[4] These authors claim that under the proper conditions a quantitative precipitation of the colloidal silica is obtained by addition of gelatin. This procedure would obviate the usual one, which involves evaporation to dryness, heating of the residue, and evaporation of the filtrate (see pp. 400–403).

PROBLEMS

1. In the precipitation of silver with an excess of iodide, part of the silver iodide remains in colloidal solution. How could the suspension be flocculated? How should the precipitate be washed to obtain a pure precipitate after ignition?

2. A solution containing ferric iron, magnesium, and sulfate is to be analyzed. Ferric iron interferes in the sulfate and magnesium determinations and must be removed by precipitation as hydrous oxide. The latter can be precipitated from a weakly acid or from an ammoniacal solution. Which condition should be selected?

3. Barium chromate precipitated under ordinary conditions consists of very fine particles. How could one proceed to get crystals of larger size?

4. Zinc sulfide can be precipitated from neutral or alkaline medium by the addition of an excess of alkali sulfide, or from weakly acid medium (pH 3 to 4) by hydrogen sulfide. Under what conditions is the coarser precipitate to be expected?

---

[1] J. R. Caldwell and M. V. Moyer, Ind. Eng. Chem., Anal. Ed. *7*, 385 (1935); J. R. Caldwell, J. Am. Chem. Soc. *57*, 96 (1935); see also W. Wepritzkaja in Z. anal. Chem. *111*, 287 (1937–38).

[2] J. R. Caldwell and H. V. Moyer, J. Am. Chem. Soc. *57*, 2372 (1935).

[3] N. F. Michailowa, Chem. Zentralbl. *110*, I, 4507 (1939).

[4] L. Weisz and H. Sieger, Z. anal. Chem. *119*, 245 (1940).

CHAPTER VIII

COPRECIPITATION PHENOMENA

Precipitates separating from a solution are not as a rule pure but contain greater or lesser amounts of foreign substances, including mother liquor. The contamination of a precipitate by substances that are normally soluble under the conditions of the precipitation is called *coprecipitation.* Contamination as a result of coprecipitation should be distinguished sharply from contamination as a result of a purely chemical precipitation (also postprecipitation, p. 113). Thus when barium chloride is added to a solution of potassium sulfate, the precipitate of barium sulfate formed is found, after washing, to contain greater or lesser amounts of potassium sulfate in spite of the fact that this salt is freely soluble under the circumstances. On the other hand, passage of hydrogen sulfide into a solution of a copper salt containing a trace of lead leads to the formation of a precipitate of copper sulfide contaminated by lead, but this contamination is not the result of coprecipitation of lead; on the contrary it is due to the *precipitation* of lead as sulfide. In studying the problems of obtaining pure precipitates, it is desirable to make a systematic classification of the various types of coprecipitation. Such a classification is given below.[1]

Classification of coprecipitation phenomena.

1. *Coprecipitation.*

(1) *Adsorption at the surface of particles exposed to the solution.* The impurity in this case is on the surface but not within the precipitate. The adsorptive properties of an ionic precipitate (i.e., a precipitate having an ionic lattice) are discussed in a subsequent section of this chapter (p. 115). Contamination by surface adsorption becomes of practical importance when precipitates having a large surface development, such as the colloidal precipitates (silver halides, hydrous oxides), are dealt with.

---

[1] Cf. I. M. Kolthoff, J. Phys. Chem. *36*, 860 (1932).

(2) *Occlusion by incorporation of foreign ions (and solvent) during the formation of the precipitate. This kind of coprecipitation is quite general and of great analytical importance.* If the incorporated material fits in the crystal lattice of the precipitate (host crystal), it is occluded in the form of *mixed* crystals or a solid solution (examples of mixed crystal formation: $BaSO_4 + PbSO_4$; $BaSO_4 + BaCrO_4$; $AgBr + AgCl$; $MgNH_4PO_4 \cdot 6\,H_2O + MgNH_4AsO_4 \cdot 6\,H_2O$). If the coprecipitated component does not fit into the crystal lattice of the precipitate, it is adsorbed during the growth of the primary particles to larger dimensions and forms the seat of imperfections in the crystal lattice of the crystalline precipitate. If these crystals are given an opportunity to become more perfect by subjecting them to repeated recrystallization (aging, see p. 104 and p. 122), the coprecipitated impurities, which do not fit in the lattice, are expelled and a much purer precipitate results.

If the impurity is present in the precipitate in the form of a mixed crystal, the aging (repeated recrystallization) does not lead to a complete expulsion of the foreign material but ultimately to a state of equilibrium between the mixed crystals and the supernatant liquid. The distribution of the mixed-crystal-forming impurity between the solid and the solution at the state of equilibrium is given by a simple expression.

Let us consider as an example the mixed-crystal formation between barium sulfate and lead sulfate. The lead ions have about the same size as the barium ions and can replace the latter in the lattice of barium sulfate:

$$BaSO_4 + Pb^{++} \rightleftarrows PbSO_4 + Ba^{++}.$$

When the system is in equilibrium, the following distribution expression is found to hold within wide limits of mole percentages of lead in the precipitate:

$$\frac{[\text{Ba}]\text{ solution}}{[\text{Ba}]\text{ precipitate}} = D\,\frac{[\text{Pb}]\text{ solution}}{[\text{Pb}]\text{ precipitate}} \qquad (1)$$

in which D is the distribution coefficient.

When the precipitation occurs under analytical conditions, distribution *equilibrium* is hardly ever attained. The distribution is quite different[1] from that in expression (1), and the amount of the coprecipitated mixed-crystal-forming impurity depends greatly upon the conditions during the precipitation.[2] In this respect the same qualitative rules (see p. 120) of coprecipitation hold for cases where the coprecipitated component is incorporated in the form of a mixed-crystal and where it is incorporated as an imperfection in the crystal lattice.

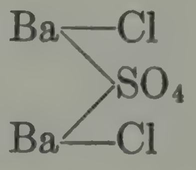
---

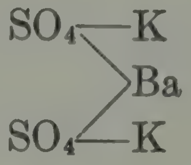
[1] H. A. Doerner and W. H. Hoskins, J. Am. Chem. Soc. *47*, 662 (1928).

[2] For the coprecipitation of lead with barium sulfate see I. M. Kolthoff and G. E. Noponen, J. Am. Chem. Soc. *60*, 197, 508 (1938); for coprecipitation of chloride with silver bromide see Kolthoff and F. T. Eggertsen, *ibid.* *61*, 1036 (1939).

It should be emphasized, however, that drastic aging may result in a pure precipitate when the original contaminant does not fit in the crystal lattice, whereas in the case of mixed-crystal formation distribution according to expression (1) is approached on aging.

(3) *Chemical-compound formation.* The presence of impurities in precipitates is often attributed to the formation of definite chemical compounds with the "host" crystal. The presence of barium chloride or potassium sulfate in barium sulfate is often ascribed to the formation of double compounds:





Actually the formation of such chemical compounds occurs very rarely and is hardly of any analytical interest.

Precipitates of varying chemical composition may separate when the central atom has a definite number of coördinated groups, one group being replaceable by another chemical group. Consider, for example, a trivalent hydrous oxide like $Al(OH)_3 \cdot xH_2O$. The precipitate formed upon slow addition of a base to a solution of an aluminum salt does not necessarily have this composition but may be a compound of the type $Al^{3+}[(OH^-)_y A^{-1}_{(3-y)}] \cdot xH_2O$ or $Al^{3+}[(OH^-)_y A^{-2}_{\frac{3-y}{2}}] \cdot xH_2O$ or $Al^{3+}[(OH^-)_y A^{-3}_{\left(\frac{3-y}{3}\right)}]$ in which A^{-1}, A^{-2}, and A^{-3} denote uni-, di-, and trivalent ions respectively. The products formed are of an amorphous nature and are not well-defined chemical compounds; the ratio of hydroxyl and anions in the precipitate may vary within wide limits.[1] It is not easy to distinguish experimentally between these substituted coördination compounds and the hydrous oxides which contain the anion A by adsorption of the acid HA.

There are rare cases in which a precipitant first yields a precipitate of the expected chemical composition, which reacts with an excess of reagent to form a double salt. Thus, on precipitation of lanthanum with alkali oxalates, $La_2Ox_3 \cdot xH_2O$ separates. With an excess of alkali oxalate, double oxalates of the type $La_2Ox_3 \cdot (Alk)_2Ox \cdot yH_2O$ are formed.[2] Similarly, in the precipitation of oxalate with lead chloride or bromide, PbOx first precipitates and then forms a double compound $PbOx \cdot Pb(Hal)_2$ with an excess of reagent.[3]

Indication of chemical-compound formation with the reagent is derived from the fact that the amount of "coprecipitation" is small when the excess of reagent is small and that it increases rapidly with increasing excess of precipitating agent. Strictly speaking, the formation of a new compound with excess of reagent is not a phenomenon of coprecipitation, but of postprecipitation, which is discussed in the next paragraph.

---

[1] Cf. G. Jander and K. F. Jahr, Kolloid Beih. *43*, 295 (1936); A. Thomas and R. D. Vartanian, J. Am. Chem. Soc. *57*, 4 (1935); T. H. Whitehead, J. P. Clay, and C. R. Hawthorne, *ibid.* *59*, 1349 (1937).

[2] I. M. Kolthoff and R. Elmquist, J. Am. Chem. Soc. *53*, 1232 (1931).

[3] Z. Karaoglanow and B. Sagortschev, Z. anorg. allgem. Chem. *199*, 7 (1931).

2. *Postprecipitation.* In this case the primary precipitate separates in a more or less pure form, and a second phase (of foreign substance) which is slightly soluble slowly forms afterwards. This second phase is therefore not coprecipitated but *postprecipitated.* Postprecipitation can occur only when the supernatant liquid is supersaturated with respect to some component which crystallizes fairly slowly. In the precipitation of calcium as oxalate in the presence of magnesium, a small amount of the latter is actually coprecipitated with the calcium oxalate. However, if the suspension is digested for a long time before filtration, some magnesium may precipitate as magnesium oxalate and contaminate the calcium oxalate precipitate (see p. 355).

The phenomena of postprecipitation are of extreme importance in the separation of metals from each other by means of hydrogen sulfide. In qualitative as well as quantitative analysis we make use of the fact that metals belonging to the "second group" (mercury, copper, etc.) form sulfides insoluble in dilute mineral acids, whereas those of the third group (zinc, manganese, etc.) are not precipitated from dilute acid medium by hydrogen sulfide. From the solubility product and the hydrogen-ion concentration (cf. p. 63), the amount of a given metal sulfide dissolved in a solution of a certain acidity saturated with hydrogen sulfide can be calculated. Thus we find that in a solution which is 0.1 N with respect to hydrogen ions the amount of dissolved zinc sulfide corresponds to about $5 \times 10^{-5}\,M$. Nevertheless, when hydrogen sulfide is passed through a solution that is 0.01 M in zinc and 0.1 N in hydrochloric acid, no precipitate appears until after a long time of standing. The original solution saturated with hydrogen sulfide is supersaturated with respect to zinc sulfide. The latter, however, separates very slowly, since the concentration of one of the reacting ions, namely, of the sulfide ion, is extremely small and of the order of $10^{-21}\,M$. Finely divided substances in general will aid in overcoming the supersaturation and in this particular case will promote the precipitation of zinc sulfide. This actually happens, but the effect of most of them is extremely small.[1] The metal sulfides of the second group have a very pronounced catalytic effect on the speed of precipitation of zinc sulfide. If we have a mixture of copper or mercuric mercury and zinc in, let us say, 0.2 N sulfuric acid and pass in hydrogen sulfide, the copper or mercuric sulfide will precipitate first without carrying down any zinc (there is no coprecipitation). However the precipitated sulfide promotes the separation of zinc sulfide, and more of the latter is found in the precipitate the longer one waits before filtration. The strong promoting effect of the metal sulfides upon the precipitation of zinc sulfide is explained by the fact that they have strong adsorptive properties towards hydrogen sulfide or other sulfides (cf. p. 95 and Fig. 5).

The concentration of sulfide ions at the interface metal sulfide and solution is greater than in the bulk of the latter. Since the speed of precipitation is a function of the concentration of the reacting components, it may be expected that zinc sulfide will precipitate faster at the surface of the metal sulfide than in the bulk of the solution. Another way of explaining the promoting effect of the metal sulfides is the following: The particles have a pronounced tendency to adsorb sulfide ions, which are fixed on the surface. Hydrogen ions form the counter ions in the double layer and may be replaced by other ions (p. 95). Zinc ions in the solution may replace the hydrogen ions in the double layer and give rise to the formation of an adsorbed layer of zinc sulfide. If the solubility product of the zinc sulfide has been exceeded, it will subsequently precipitate. It separates in an extremely finely divided form; each new layer of zinc sulfide formed promotes the precipitation of more material from the solution for the reasons mentioned.

---

[1] I. M. Kolthoff and E. Pearson, J. Phys. Chem. *36*, 549 (1932).

It has been found that the promoting effect of mercuric sulfide upon the postprecipitation of zinc sulfide is extremely great; the following table[1] clearly shows how the postprecipitation increases with the time of standing under hydrogen sulfide before filtration.

TABLE XXI. POSTPRECIPITATION OF ZINC SULFIDE WITH MERCURIC SULFIDE
(25 ml. 0.05 *M* mercuric chloride, 25 ml. 0.05 *M* zinc sulfate in 0.35 *N* sulfuric acid)

TIME OF PASSING IN HYDROGEN SULFIDE IN MINUTES	TIME OF SHAKING UNDER HYDROGEN SULFIDE PRESSURE BEFORE FILTRATION IN MINUTES	PERCENTAGE OF TOTAL ZINC IN PRECIPITATE
3	0	37.3
4	10	89.2
3	20	91.5
3	60	94.5
3	30	0.1 (without $HgCl_2$ at same acidity)

In making quantitative separations of various metals at different acidities with the aid of hydrogen sulfide, one must consider the possibility of the postprecipitation of a second sulfide promoted by the freshly precipitated primary sulfide.

Adsorptive properties of precipitates having ionic lattices.

It is not our purpose here to give a complete outline of the adsorptive properties of precipitates with ionic lattices. The discussion will be limited to those properties which are of direct significance in analytical chemistry.

---

[1] I. M. Kolthoff and R. Moltzau, J. Phys. Chem. *40*, 779 (1936); postprecipitation of zinc with bismuth sulfide, see Kolthoff and F. S. Griffith, *ibid.* *42*, 531 (1938); postprecipitation of nickel with sulfides of copper, mercuric mercury, and zinc, cf. Kolthoff and Griffith, *ibid.* *42*, 541 (1938); postprecipitation of ferrous sulfide with copper sulfide, cf. Kolthoff and Griffith, J. Am. Chem. Soc. *60*. 2036 (1938).

Adsorption of salts having an ion in common with the precipitate.

Figure 6 gives a schematic cross section of a crystal having the simple structure of the sodium chloride type, the + signs representing the positive ions, the − signs the negative ions. A positive ion *A* in the interior of the crystal is subjected to the attractive forces of four neighboring negative ions, *a*, *b*, *c*, and *d*, and also of course to one directly above it and one directly below. *A*, therefore, is acted upon by the electrical forces of six surrounding negative ions. An ion *B* in the surface experiences the attractive forces of five negative ions (*e*, *a*, *f*, and two in the neighboring planes). The positive ions in the surface therefore have free residual valences by virtue of which they can attract negative ions. Preferentially they will adsorb the negative lattice ions, since the forces acting between lattice cations and anions must be great as indicated by the slight solubility; for the same reason the negative ions in the surface will attract positive lattice ions from the solution. If lattice cations present in the solution are attracted and adsorbed by the surface, an equivalent number of foreign negative ions must also be attracted to the surface, since otherwise the solution would acquire a free negative charge and the surface a free positive charge, which is impossible. As the result of such attractive forces, then, we find that a salt containing a lattice ion will be adsorbed from the solution on the surface of the precipitate. Many years ago it was shown by Lottermoser and Rothe[1] that pure silver iodide adsorbs both silver and iodide salts.

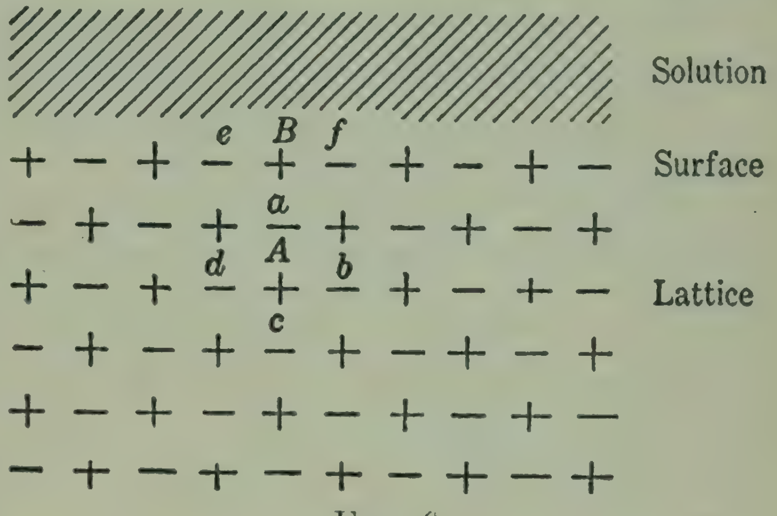


FIG. 6

Let us now consider the adsorption of various salts all having the same lattice ion in common; for example, the adsorption of barium salts by barium sulfate. Experimentally it is found that the adsorption at the same final salt concentration in solution is not the same for the various barium salts but *increases more or less with decreasing solubility of the barium salt.* The relation is formulated by the *F. Paneth-K. Fajans-O. Hahn* adsorption rule: "Those ions whose compounds with the oppositely charged constituent of the lattice are slightly soluble in the solution in question are well adsorbed by the ionic lattice." At the same final concentration in the solution it is found, for example,[2] that silver acetate is much more strongly adsorbed than silver nitrate by silver iodide, the acetate being less soluble than the nitrate. In addition to the solubility of the adsorption compound, there are other factors which determine the adsorbability. Among these the following two are of great importance: the *electrical dissociability* of the adsorbed compound and *deformability* of the adsorbed ions. The adsorption increases with decreasing dissociation of the adsorption compound. For example, hydrogen sulfide, a weak electrolyte, is strongly adsorbed by metal sulfides.

---

[1] A. Lottermoser and A. Rothe, Z. physik. Chem. *62*, 359 (1908).

[2] J. S. Beekley and H. S. Taylor, J. Phys. Chem. *29*, 942 (1925).

The adsorbability also increases with increasing deformability of the adsorbed ions. Ions do not have a rigid structure, and it is possible by application of electrical forces to deform the shell of the outer electrons. Anions as a rule are more easily deformed than cations; the deformability of the former increases with increasing size of the ions. Anions of the large aromatic molecules (dyes) especially are distinguished by great deformability. Use is made of this fact in the application of adsorption indicators in volumetric analysis (cf. p. 473 where the mechanism of the action of adsorption indicators is discussed). *From the viewpoint of coprecipitation it is most important to remember that a precipitate adsorbs salts containing the lattice cation or lattice anion and that the adsorbability as a rule increases with decreasing solubility and decreasing electrolytic dissociation of the adsorbed compound.*

Adsorption of salts having no ion in common with the precipitate. Exchange adsorption.

It was explained above that the ions in the surface of an ionic lattice exhibit residual valence forces. The negative ions in the surface therefore attract positive ions from the solution, and the positive ions attract negative ions. Therefore it might be expected that a salt having no ion in common with the precipitate would be adsorbed as such on the surface. Actually another process may take place as well.

In a discussion of the effect of aging upon the structure of a precipitate, the process of kinetic exchange was mentioned (p. 105). Equilibrium between the precipitate and the surrounding solution means that the speed with which lattice ions leave the surface is equal to the speed with which ions from the solution deposit again on the surface. Let us consider what will happen when barium sulfate is shaken with a dilute solution of lead perchlorate. The lead ions are strongly attracted by the barium sulfate, since lead sulfate is slightly soluble and the lead sulfate fits into the lattice of barium sulfate. The perchlorate ions, on the other hand, have no pronounced tendency to be adsorbed, since the barium perchlorate is very easily soluble. Let us assume that *e* and *B* in Figure 6 represent a sulfate and a barium ion respectively and that at a certain moment both leave the surface and go into the solution. There will be a pronounced tendency for ions to be deposited again at this vacant spot. Both barium and lead ions are strongly attracted by the lattice, and it may happen that a lead ion deposits at *B* instead of a barium ion. The sulfate ions, on the other hand, are much more strongly adsorbed than the perchlorate ions, and the former will be deposited at *e*. Therefore on shaking barium sulfate with a very dilute lead perchlorate solution the following *surface* reaction takes place:

$$\underset{(surface)}{BaSO_4} + \underset{(solution)}{Pb^{++} + 2\,ClO_4^-} \rightleftarrows \underset{(surface)}{PbSO_4} + \underset{(solution)}{Ba^{++} + 2\,ClO_4^-}.$$

As a result of this surface reaction, barium ions in the surface are partly replaced by lead ions, i.e., the latter are adsorbed, and an equivalent amount of barium ions enters the solution. This exchange adsorption takes place in spite of the fact that the solubility product of lead sulfate is not exceeded. It has been shown[1] that on shaking calcium oxalate monohydrate with dilute solutions of alkali iodate, sulfate, and hydroxide respectively, the foreign anions can replace some of the oxalate ions in the surface, no cation adsorption taking place:

$$\underset{(surface)}{\mathrm{CaOx}} + \underset{(solution)}{\mathrm{SO_4^=} + 2\,\mathrm{K^+}} \rightleftarrows \underset{(surface)}{\mathrm{CaSO_4}} + \underset{(solution)}{\mathrm{Ox^=} + 2\,\mathrm{K^+}}.$$

With dilute solutions of barium and manganese chlorides a cation exchange is found:

$$\underset{(surface)}{\mathrm{CaOx}} + \underset{(solution)}{\mathrm{Ba^{++}} + 2\,\mathrm{Cl^-}} \rightleftarrows \underset{(surface)}{\mathrm{BaOx}} + \underset{(solution)}{\mathrm{Ca^{++}} + 2\,\mathrm{Cl^-}}.$$

Quite generally, therefore, there is a competition between lattice ions and foreign ions of the same electrical sign to be adsorbed at the surface of a precipitate. The less soluble the compound formed between the foreign ion and the lattice ion of opposite sign, the greater is the probability that the former will replace the lattice ion. This conclusion is of importance in the correct interpretation of occlusion phenomena.

Exchange between foreign ions absorbed at the surface of impure precipitates and other ions in the solution.

In a discussion of the properties of colloidal solutions (p. 95) we saw that the particles are kept in colloidal solution by the adsorption of their own ions on the surface.

By adding silver nitrate solution to 0.01 N potassium iodide (not enough to precipitate all the iodide), a stable colloidal solution of silver iodide is obtained. The particles are kept in colloidal solution by a primary adsorption of iodide ions, and an equivalent amount of potassium ions is present as "counter ions." By addition of sufficient electrolyte, say potassium nitrate, the sol is flocculated. The fresh precipitate still contains adsorbed potassium iodide, which is hard to remove by washing. The "counter ions," in this case potassium ions, can be replaced by other ions present in the solution. If the precipitate is washed with a dilute solution of sulfuric acid, for example, they are replaced by hydrogen ions:

$$\underset{(particle)}{\mathrm{AgII^-}\,\vdots\,\mathrm{K^+}} + \mathrm{H^+} \rightleftarrows \mathrm{AgII^-}\,\vdots\,\mathrm{H^+} + \mathrm{K^+}.$$

($\mathrm{AgII^-}\,\vdots$ denotes adsorbed iodide fixed on the surface of the silver iodide; $\mathrm{K^+}$ is the counter ion.)

Ammonium ions have, qualitatively, the same effect as hydrogen ions. If the precipitate has been thoroughly washed with a solution of an acid or an ammonium salt, it still may contain adsorbed iodide in the form of hydrogen or ammonium iodide. Since these two are easily volatilized, a pure precipitate results on heating.

---

[1] I. M. Kolthoff and E. B. Sandell, J. Am. Chem. Soc. *55*, 2170 (1933); *59*, 1543 (1937). See also Kolthoff and Ch. Rosenblum, *ibid.* *55*, 2664 (1933)

Adsorption of solvent (water) by precipitates. Hygroscopic water.

Molecules which have a polar character (dipoles) are attracted by the ions in the surface of a crystal lattice and are held there very strongly. An air-dried precipitate, for example, always contains some adsorbed water, which may be called water of hygroscopicity. The amount of water adsorbed increases with increasing surface development of the precipitate, the adsorption taking place on both the external and internal surfaces. Certain authors recommend weighing precipitates in the air-dry form by proceeding as follows: After the ordinary washing process, the precipitate is washed with alcohol, which is followed by ether. Air is then drawn through to remove the ether, and the precipitate is weighed. Under these conditions one is liable to find high results, owing to the adsorption of water vapor and also to occlusion of water. Thus it has been found [1] that calcium oxalate monohydrate precipitated under ordinary analytical conditions (dilute weakly acidic solutions, precipitation at 100°) contains as much as 1 per cent of hygroscopic water in the air-dry state. This water is partially removed by heating to 105°–110° but is readily taken up again when the precipitate is exposed to the air. If the total surface of the precipitate is decreased by digestion at higher temperatures (recrystallization accompanied by perfection of crystals, p. 104 and p. 122) the amount of hygroscopic water decreases proportionally. Barium sulfate loses adsorbed water readily at 100°, but occluded water is removed slowly at temperatures below 500°.

The interpretation of coprecipitation. Surface adsorption. Colloidal precipitates.

Surface adsorption can be responsible for marked contamination if the precipitate has a large exposed surface. This is the case when it separates as a flocculated colloid (metal sulfides, hydrous oxides, silver halides). In these cases one of the ions of the precipitate is primarily adsorbed (cf. p. 95 and Fig. 5), thus dragging an equivalent amount of foreign ions to the surface. If silver, for example, is precipitated with an excess of potassium chloride, the precipitate will contain some of the latter adsorbed. On washing with dilute acid or ammonium salts, the potassium is replaced by hydrogen or ammonium, and the adsorbed chloride volatilizes on heating the precipitate. Silver bromide formed by precipitation with an excess of silver contains some silver salt adsorbed which cannot be eliminated by washing with a suitable electrolyte solution and subsequent ignition, since none of the silver salts is volatile. Washing with water does not remove all the adsorbed electrolyte. Under these conditions a marked decrease in the amount of adsorbed material is obtained if the precipitate is subjected to an aging process by digestion at higher temperatures. The total surface decreases markedly as a result of recrystallization of the particles. Such an aging process as a rule results in a decrease in the amount of adsorbed electrolytes. Silver chloride ages very rapidly even at room temperature. Ten minutes after the precipitation it does not exert noticeable adsorptive properties towards silver nitrate.

---

[1] E. B. Sandell and I. M. Kolthoff. J. Phys. Chem. 37, 153 (1933).

Amorphous precipitates, such as hydrous oxides of aluminum and ferric iron, when formed with an excess of ammonia in the presence of copper, zinc, magnesium, etc., give a primary adsorption of hydroxyl ions, with a simultaneous adsorption of one of the other ions mentioned. The precipitate is badly contaminated by surface adsorption.[1] Virtually the same contamination is found if the hydrous oxides are precipitated in the absence of the other metals and copper, zinc, etc., are added immediately afterwards. This shows that we are dealing with a surface adsorption. It is very difficult to remove the adsorbed divalent metals from the surface of the hydrous oxides. It is often recommended to make the precipitation in strongly ammoniacal medium in the presence of a large amount of an ammonium salt and to wash the precipitate with a solution of the latter. A much purer precipitate is obtained under these conditions, since the ammonium ions replace part of the adsorbed metal ions on the surface. If it is impossible to prevent the adsorption of interfering elements, one must dissolve the precipitate and reprecipitate it one or more times.

Reprecipitation is a powerful means of obtaining purer precipitates. In the first precipitation only a small fraction of the total amount of the contaminating constituent is carried down. Upon dissolving and reprecipitating, the concentration of the contaminant in the solution is much smaller than in the original. Again a fraction of the amount still present is carried down upon precipitation, which naturally is much smaller than the amount coprecipitated in the first precipitation. In many cases the amount of impurity carried down in the second precipitation is so small that it may be neglected. However, it should not be inferred that a reprecipitation always leads to precipitates of adequate purity.[2] Generally, the percentage adsorption is much greater at small than at large concentrations of the contaminant. The change of the amount adsorbed with the concentration is determined by the so-called adsorption isotherm. Empirically it has been found that within a certain range of concentration the following relation exists between the amount adsorbed (x) by a given weight of adsorbent and the final concentration of the adsorbate in the solution (c):

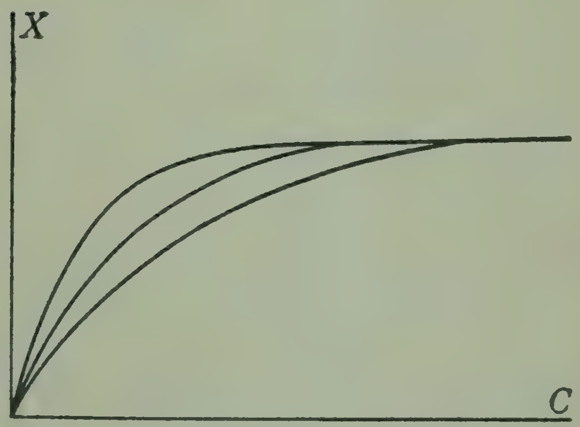


FIG. 7. Adsorption isotherms of solutes.

$$x = \alpha c^{1/n}$$

---

[1] I. M. Kolthoff and B. Moskovitz, J. Phys. Chem. *41*, 629 (1937); Kolthoff and L. Overholser, *ibid. 43*, 767, 909 (1939).

[2] For a graphical and mathematical treatment see T. B. Smith, *Analytical Processes*, 2d ed., p. 133, E. Arnold and Co., London, 1940.

in which α and n are constants. The adsorption isotherm in general has the shape given in Figure 7.

Occlusion: adsorption during the growth of the precipitate. Kind of coprecipitation. Occlusion of foreign cations or foreign anions.

If a precipitate such as barium sulfate is formed in the presence of an excess of a barium salt, say barium chloride, it will adsorb barium ions at its surface during the growth of the crystals. Owing to the electroneutrality of both phases, an equivalent amount of chloride ions must be dragged to the surface with the barium ions. If the precipitate is formed under such conditions that the crystals grow very slowly, the sulfate ions in the solution will replace most of the chloride, and the occlusion of barium chloride will be small. If, on the other hand, the crystals grow rapidly, as is usually the case in the precipitation of slightly soluble substances, there will be no time available for a complete exchange between the contaminating ions and the sulfate ions, and a larger coprecipitation will result. If the coprecipitation of different kinds of anions is compared, one must realize that their adsorbability, and therefore their occlusion also, is roughly determined by the Paneth-Fajans-Hahn adsorption rule. In general the less soluble the barium salt the more it will be occluded by barium sulfate. However, it is emphasized that in addition to solubility other factors determine the adsorbability. Nitrate is more strongly occluded than chloride, since barium nitrate is less soluble than the chloride. If barium sulfate is precipitated from solutions containing an excess of sulfate, the foreign anions are given less opportunity to be adsorbed and occluded, since a primary adsorption of sulfate ions may be expected Under these conditions the occlusion of foreign cations will predominate, the adsorbability and occlusion again being determined to a large extent by the Paneth-Fajans-Hahn adsorption rule. From the above it follows that if one wishes to cut down the coprecipitation of anions with barium sulfate, the precipitation should be carried out in a medium containing an excess of sulfate.

It is well known that ferric iron gives a very pronounced coprecipitation in the determination of sulfate as barium sulfate. The salts of ferric iron are strongly hydrolyzed in aqueous medium and contain many colloidal particles of positively charged hydrous ferric oxide. If the sulfate solution containing the iron is slowly precipitated with barium salt, the primary precipitate acquires a negative charge by adsorption of sulfate ions. The negative and positive particles attract and flocculate each other, and therefore a strong occlusion of iron occurs. The hydrolysis of the ferric iron salt is repressed by the addition of strong acid; most of the iron is then present in the form of ferric ions (or complexes). The amount of coprecipitation decreases in the presence of acid but is not completely eliminated, since the ferric ions are adsorbed by the growing particles. If the sulfate solution containing iron is added to an excess of an acid barium chloride solution, the iron is not given much chance to be adsorbed, and a precipitate practically free from iron is formed.

From the above it should not be concluded that foreign anions are coprecipitated only when an excess of the lattice cation is present during the precipitation (or foreign cations when there is an excess of lattice anions) and that no occlusion of anions can occur when the lattice anions are in excess during the precipitation. In the discussion of the adsorptive properties of ionic lattices (p. 114) we saw that there is competition between lattice ions and foreign ions of the same electrical sign to be adsorbed at the surface. Iodate ions, for example, are adsorbed by calcium oxalate; calcium ions promote the adsorption, oxalate ions inhibit it. Still there is a slight adsorption of iodate ions in the presence of an excess of oxalate ions. Consequently it is found that iodate ions are relatively strongly occluded by calcium oxalate if the latter is formed in a medium containing an excess of calcium; the occlusion is decreased strongly, but not reduced to zero, if the precipitation is made in a solution containing an excess of oxalate ions.

Summarizing then, we have the following rules to guide us in predicting the kind and amount of occlusion:

1. *Occlusion of foreign cations may be expected to predominate when the solution contains an excess of lattice anions during the precipitation. The amount of occlusion increases with increasing concentration of lattice anions and decreases (sometimes to zero) if the precipitation is made from a solution containing an excess of lattice cations. The reverse rule holds for the coprecipitation of foreign anions.*

2. *Under identical conditions the coprecipitation of foreign ions is of the same order as their adsorbability on the surface of the precipitate.*

A few examples of the coprecipitation of foreign cations and anions with calcium oxalate monohydrate [1] which demonstrate the general validity of the above rules are given below. The order of the adsorbability of the alkali oxalates by calcium oxalate was experimentally found to be $Na^+ > K^+ = NH_4^+$. In agreement herewith, the coprecipitation decreases in the same order. In the precipitation of calcium oxalate at 100° in the presence of the same number of equivalents of alkali chlorides, the following occlusion was found:

Excess of calcium during precipitation: Occluded alkali oxalate in millimoles per gram of calcium oxalate:

0.037 Na; 0.0051 K; 0.0064 NH_4^+.

Excess of oxalate during precipitation:

0.064 Na; 0.0072 K; 0.0083 NH_4^+.

The coprecipitation of chloride, bromide, and iodide with calcium oxalate is extremely small under all conditions. This is to be expected, since the calcium halides are very soluble and therefore their adsorbabilities are very small. Hydroxide, sulfate, and iodate are occluded as could be expected. In the precipitation of calcium oxalate at 100° in the presence of 2 g. of ammonium sulfate, an occlusion of 13.0 mg. of calcium sulfate per gram of calcium oxalate was found when the precipitation was made in the presence of an excess of calcium, whereas only 5.3 mg. of sulfate were occluded in the presence of an excess of oxalate.

---

[1] See I. M. Kolthoff and E. B. Sandell, J. Phys. Chem. *37*, 443, 459 (1933).

The coprecipitation of calcium hydroxide with calcium oxalate is of practical importance. If the calcium oxalate is precipitated from ammoniacal or even from neutral medium, an occlusion of calcium hydroxide occurs. If the precipitate is weighed in the form of oxide or sulfate, the hydroxide occlusion does not interfere with the calcium determination. However, if the precipitate is titrated with permanganate, low results will be found, since part of the calcium is present as hydroxide and not as oxalate. Precipitation from weakly acid medium (acetic acid and ammonium acetate) prevents the occlusion of hydroxide but may result in a coprecipitation of oxalic acid or bioxalate.

The effect of the kind of lattice ion present in excess during the precipitation of barium sulfate upon the occlusion of anions is clearly demonstrated by experiments of Weiser and Sherrick:[1]

Occlusion of:	Cl^-	Ba^{++}	in excess:	1.58	g. eq. per 100 moles of $BaSO_4$.
" "	"	$SO_4^=$	" "	0.125	" " " " " " "
" "	ClO_3^-	Ba^{++}	" "	5.84	" " " " " " "
" "	"	$SO_4^=$	" "	2.27	" " " " " " "
" "	MnO_4^-	Ba^{++}	" "	2.85	" " " " " " "
" "	"	$SO_4^=$	" "	1.37	" " " " " " "

Amount of coprecipitation.

The amount of coprecipitation is determined in the first place by the adsorbability of the foreign ion (Paneth-Fajans-Hahn rule). In addition the amount of occlusion of a *given ion* is determined by the following factors:

1. *The speed of formation of the precipitate*, which in turn is a function of the concentration of the ion being precipitated and the concentration of the precipitating agent, the manner of mixing the two solutions, the presence of foreign substances affecting the solubility (e.g., acids), and the temperature during the precipitation. If the precipitate is formed by mixing very concentrated solutions at room temperature, it separates as a more or less flocculated colloid which is likely to be badly contaminated, especially by surface adsorption.

If the precipitate is formed from fairly dilute solutions, especially at higher temperatures (analytical conditions), the growth still takes place fairly rapidly, and as a rule microscopic crystals are formed. The conditions of formation of such precipitates are very favorable for occlusion: adsorption takes place during the growth of the crystals, and there is no adsorption equilibrium.

If the precipitate is formed extremely slowly, it yields large, sometimes macroscopic, crystals. These have grown so slowly that adsorption equilibrium was attained at the new planes formed during the crystal growth. Such precipitates are usually purer than those formed under the classical analytical conditions (former case).

2. *The treatment of the precipitate before filtration.* In the chapter on the "Formation and Properties of Precipitates," it was mentioned that the particles of a crystalline precipitate which has been formed rapidly are far from perfect and are subject to repeated recrystallization when the precipitate is aged in the mother liquor or in another suitable liquid

---

[1] H. B. Weiser and J. L. Sherrick, J. Phys. Chem. 23, 205 (1919).

medium. During the repeated recrystallization the foreign coprecipitated material has an opportunity to enter the solution. Since the continuous recrystallization process is slow as compared to the speed of formation of the original precipitate, there is an opportunity for the attainment of adsorption equilibrium during the aging. A very finely divided and extremely imperfect precipitate is obtained when the precipitation takes place from very concentrated solutions at room temperature. Such a precipitate, which contains a considerable amount of contaminants including water, is subjected to many recrystallizations when it is aged in a liquid medium, especially at higher temperatures. Consequently, such an aging results in an expulsion of the impurities and in the formation of a relatively pure precipitate. Under ordinary analytical conditions precipitates are produced by slow addition of the reagent to a hot, dilute solution of the substance to be precipitated. Such precipitates are much less imperfect than those obtained by mixing concentrated solutions at room temperatures. The speed of recrystallization of such precipitates when aged at higher temperatures is much less than that of precipitates formed from concentrated solutions. Still, those precipitates formed under the ordinary analytical conditions are subject to recrystallization when aged. Therefore, aging on a steam bath or a hot plate quite generally results in a purification of the original precipitate. A few examples substantiate the above rule. The following figures show the gradual removal of adsorbed and occluded sodium sulfate from 2 g. of barium sulfate when this was allowed to stand in the mother liquor at 20°: [1]

Coprecipitated Na_2SO_4 in mg.	22.6	19.0	17.4	14.0	10.4	8.2	7.6
Time of standing	15 min.	3 hrs.	18 hrs.	2 days	48 days	5 mos.	7 mos.

The beneficial effect of aging upon the removal of nitrate coprecipitated with lead sulfate was shown by Kolthoff and Halversen.[2] The following figures illustrate clearly the effect of aging under favorable conditions. Ten ml. of 0.1 M sodium sulfate were added quickly to 10.5 ml. of 0.1 M lead nitrate at room temperature. The fresh precipitate contained 0.64 per cent coprecipitated nitrate. Upon aging at 95° in the supernatant liquid, which was made 0.01 N in nitric acid, the percentage of nitrate in the precipitate was 0.12 after 1 hour, 0.04 after 6 hours, and 0.01 after 24 hours.

The rule that aging under favorable conditions results in the formation of a much purer precipitate or sometimes of a precipitate free of impurities does not hold when:

a. The contaminant forms a mixed crystal with the host crystal (precipitate). In such a case the final precipitate obtained upon drastic aging contains the mixed-crystal-forming contaminant in distribution equilibrium with the solution (p. 111). The mixed-crystal-forming contaminant could be more or less completely eliminated if the supernatant liquid were removed after the precipitation and the aging carried out in a medium free from this constituent.

---

[1] Mellor, *A Treatise on Quantitative Inorganic Analysis*, 1st ed., p. 614, Griffin, 1913, quoted by T. B. Smith, *Analytical Processes*, 2nd ed., p. 53 (1940).

[2] I. M. Kolthoff and R. A. Halversen, J. Phys. Chem. *43*, 605 (1939).

b. The contaminant slowly forms a chemical compound with the original precipitate. This rare case was met with in the aging of ferric hydroxide in ammoniacal medium in the presence of several divalent cations.[1] Apparently, these cations are able to form ferrites with ferric hydroxide even at relatively low temperatures. Some typical figures are given in Table XXII, in which the precipitate was formed at room temperature and aged at 98°.

TABLE XXII. CHANGE OF COPRECIPITATION OF DIVALENT METALS WITH FERRIC HYDROXIDE UPON AGING AT 98°

(The final metal concentration was 0.02 *M*, and the supernatant liquid 0.90 *M* in ammonia and 0.077 *M* in ammonium chloride.)

TIME OF AGING AT 98°	ZINC COPPT. IN %	NICKEL COPPT. IN %	COBALT COPPT. IN %	MAGNESIUM COPPT. IN %	CALCIUM COPPT. IN %
Fresh	18.3	14.3	17.4	15.1	12.9
15 minutes	24.1				
30 minutes		37	33		
5 hours	35	51	58.5	14.0	4.0
2 days	52.4			12.1	

It is seen that the amounts of coprecipitated zinc, nickel, and cobalt rapidly increase upon aging at 98°; the amount of coprecipitated magnesium decreases very slightly, whereas the amount of coprecipitated calcium decreases considerably. Apparently, the calcium does not form a ferrite under the experimental conditions.

The effect of conditions of formation and of digestion upon the purity of a precipitate have been clearly demonstrated in studies on coprecipitation with calcium oxalate.[2] As an example, some experiments on the coprecipitation of iodate are given in the following table. The effect of the presence of an excess of calcium or oxalate during the precipitation upon the occlusion of iodate is demonstrated in the first eight experiments. By precipitation at 100° from fairly dilute solutions a finely divided precipitate is obtained (experiments 3 and 4; size $< 1\ \mu$). By carrying out the precipitation at "extreme dilutions," much larger crystals which can be filtered very easily (experiments 7 and 8) are obtained. However, they usually contain more occluded iodate than precipitates formed more rapidly (compare 1 and 2 with 5 and 6, respectively).

A comparison of the results of experiments 1 and 2 with 9 and 10 respectively shows the beneficial effect of digestion. The primary particles (experiments 1 and 2) were subjected in the process to a drastic recrystallization (transformation of hydrates). The precipitate formed in experiment 4 underwent incomplete recrystallization on digestion (experiment 11) but nevertheless was much purer after the aging as a result of the slow recrystallization and the perfection of the other particles which did not grow in size. The precipitate formed in experiment 7 was composed of such coarse crystals that no recrystallization took place on digestion. Nevertheless, the amount of occluded iodate diminished to about one half of the original value, owing to the perfection that occurred.

---

[1] I. M. Kolthoff and L. Overholser, J. Phys. Chem. *43*, 767, 909 (1939).

[2] I. M. Kolthoff and E. B. Sandell, *loc. cit.*

TABLE XXIII. COPRECIPITATION OF IODATE WITH CALCIUM OXALATE UNDER VARIOUS CONDITIONS

METHOD OF PRECIPITATION AND TREATMENT	AVERAGE SIZE OF CRYSTALS IN μ	MILLIMOLES IODATE IN 1 G. CALCIUM OXALATE MONOHYDRATE
1. Oxalate to excess calcium; room temp.	0.5	0.017
2. Calcium to excess oxalate; room temp.	0.5	0.011
3. Oxalate to excess calcium; 100°	1	0.044
4. Calcium to excess oxalate; 100°	1	0.028
5. Extreme dilution;[a] calcium in excess; room temp.	*ca.* 2	0.075
6. Extreme dilution; oxalate in excess; room temp.	2	0.09
7. Extreme dilution; calcium in excess; 100°	5	0.06
8. Extreme dilution; oxalate in excess; 100°	4–10	0.017
9. As in 1, but digested for 20 hours	*ca.* 2	0.0012
10. As in 2, but digested for 20 hours	*ca.* 2	0.001
11. As in 4, but digested for 20 hours	1– 2	0.004
12. As in 7, but digested for 20 hours	*ca.* 5	0.03

[a] Precipitation at "extreme dilution" was carried out in the following way: The calcium chloride and ammonium oxalate solutions were added simultaneously from two burets to 60 ml. of water containing the potassium iodate. Either the calcium or the oxalate was kept 1 ml. in excess during the entire addition.

From the above outline one may conclude that *often* the purest precipitates are obtained in the following way: *The precipitation is made at room temperature from concentrated solutions; the suspension is diluted with water or, better, with a solution of an electrolyte in which the precipitate is more soluble than in water (to promote the speed of recrystallization) and is digested overnight on a steam bath and then filtered.* The application of this procedure to quantitative precipitations requires that possible solubility losses be taken into account.

PROBLEMS

1. Sulfate is to be determined in a solution containing calcium. Why would one expect an occlusion of calcium in the barium sulfate formed? Will this occlusion be greater if barium chloride is added slowly to the sulfate solution or if the latter is added to an excess of barium at the same rate?

2. Analyst A separates zinc from ferric iron by the addition of enough ammonia to keep all of the former in solution as the zinc ammonio ion. Ana-

lyst B prefers to use a large excess of ammonia and to add a few grams of ammonium chloride. Which is the better of the two procedures? Explain.

3. In the precipitation of barium in the presence of lead with an excess of sulfate, part of the lead is occluded by the barium sulfate in the form of mixed crystals. Lead sulfate is soluble in ammonium acetate. Explain why all of the lead cannot be extracted from the precipitate with ammonium acetate.

4. An excess of standard barium hydroxide is added to a solution of pure ferric chloride, and the mixture is diluted to the mark in a volumetric flask. An aliquot part of the supernatant liquid is back-titrated with standard acid. Does this procedure give good results? Are they low or high?

5. Copper is separated from zinc in a medium of 0.5 *N* sulfuric acid by precipitation with hydrogen sulfide. What measures would you take to eliminate or minimize the postprecipitation of zinc?

CHAPTER IX

WATER IN SOLIDS

EFFLORESCENCE AND DELIQUESCENCE. PREPARATION OF HYDRATES WITH A DEFINITE AMOUNT OF WATER OF CRYSTALLIZATION. ADSORPTION OF WATER VAPOR. ESSENTIAL AND NONESSENTIAL WATER

Vapor pressure of water, aqueous solutions, and crystal hydrates.

The pressure of water vapor in equilibrium with liquid water increases with increasing temperature as shown in the following table:

TABLE XXIV. VAPOR PRESSURE OF WATER AT VARIOUS TEMPERATURES

Temperature ° C.	0	10	15	20	25	30	35	100
Pressure, mm. of mercury	4.6	9.21	12.79	17.53	23.76	31.82	41.6	760

Dissolved substances in water decrease the aqueous tension; the water-vapor tension depends on the concentration of the solute and upon the temperature. The vapor pressure of a given solution is a constant at a given temperature but increases with increasing temperature. Suppose that increasing amounts of a salt like potassium chloride are dissolved in water, the temperature being kept constant. The water-vapor pressure will gradually decrease until the solution is saturated with the salt. Further addition of salt (solid phase) will not change the composition of the saturated solution (liquid phase); in other words, a mixture of a saturated solution of a salt with the solid has a constant vapor tension at a fixed temperature. Graphically the change of the vapor tension on going from pure water

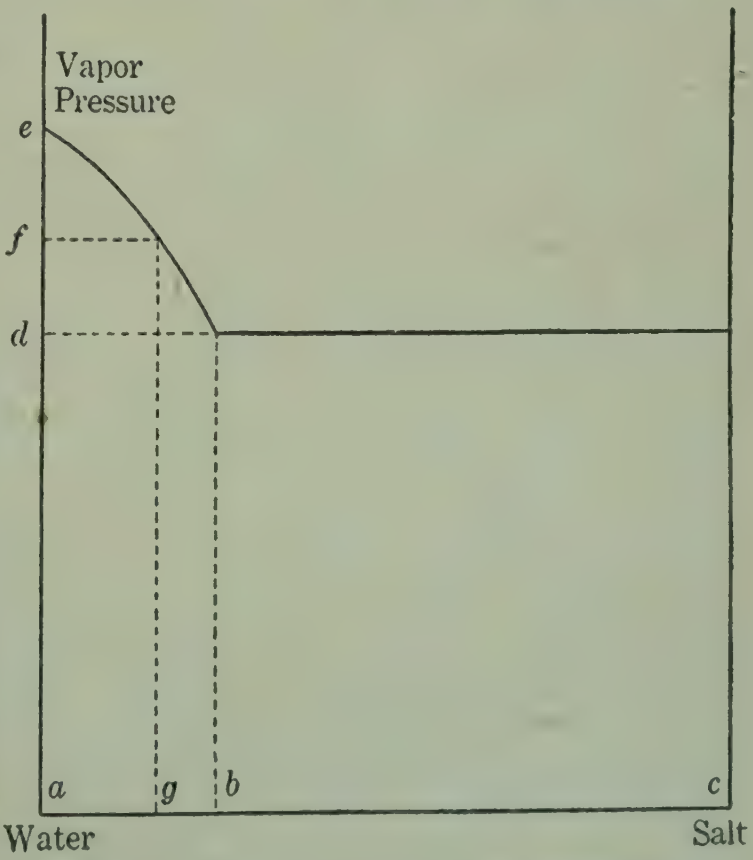


FIG. 8. Vapor pressure of water in the system water-anhydrous salt at constant temperature.

to the pure salt is shown in Figure 8. Point *a* corresponds to 100 per cent water with a vapor pressure corresponding to *ae*. Point *c* represents the pure anhydrous salt with an aqueous tension of zero. On dissolving increasing amounts of salt, the vapor tension of the water decreases from *e* to *d*; at the latter point the solution is saturated with the salt. The composition of the saturated solution is given by point *b* on the abscissa; the ratio of water to salt is equal to *bc* : *ba*. If the saturated salt solution is evaporated at constant temperature, the vapor pressure does not change until all of the water has been removed; with the removal of the last trace of the saturated solution it drops from *d* to zero.

If the solid phase is not anhydrous but a salt hydrate, the behavior is somewhat different. The water of crystallization in the hydrate exerts a certain pressure, which may be called the dissociation pressure of the hydrate. Strictly speaking, one cannot consider the vapor pressure of a single hydrate but of a system. If the hydrate represented by $S \cdot nH_2O$ yields the anhydrous form on dehydration, the splitting-off of water may be represented by the equation:

$$\underset{(hydrate)}{S \cdot nH_2O} \rightleftarrows \underset{(anhydrous\ salt)}{S} + nH_2O.$$

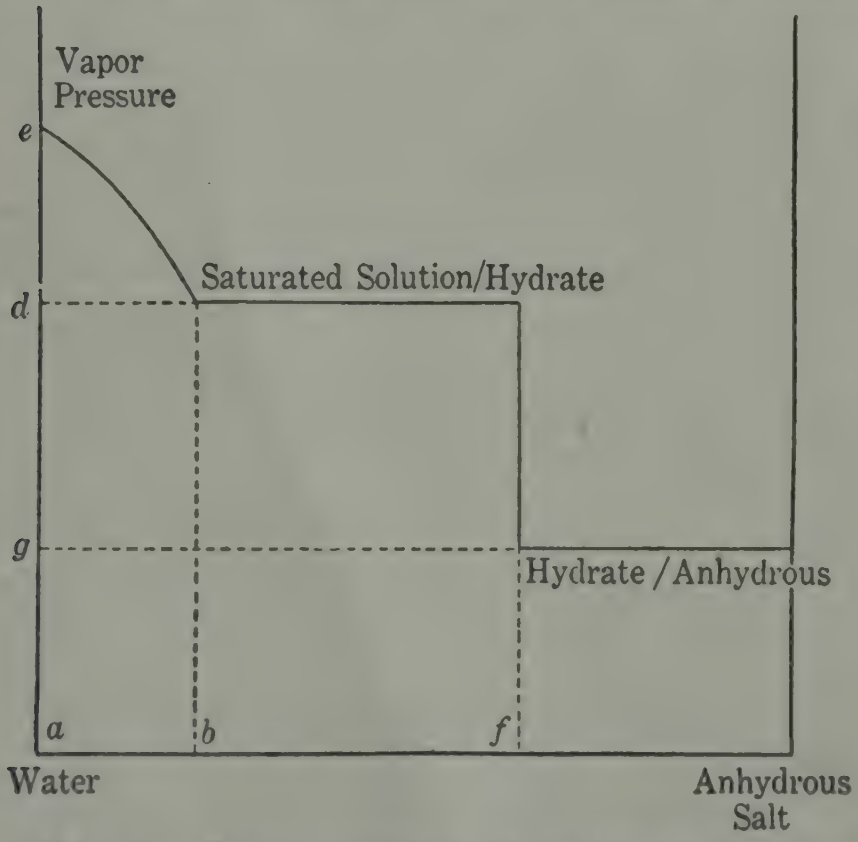


FIG. 9. Vapor pressure of water in the system water-salt hydrate-anhydrous salt at constant temperature.

Suppose that the salt hydrate is placed (at constant temperature) in a closed space in which the vapor pressure of water is equal to zero. Owing to the vapor pressure of the hydrate, a little water will be given off to the gas phase with the simultaneous formation of an equivalent amount of the anhydrous salt *S*. The aqueous tension of the vapor phase is equal to the water-vapor pressure of the salt hydrate and is constant for any mixture of the hydrate and the anhydrous form as long as the temperature remains constant. The vapor pressure of the system water-anhydrous salt at constant temperature is graphically represented in Figure 9. The vapor pressure of a saturated solution of the salt hydrate in equilibrium with the solid hydrate is represented by *d*. After removal of all of the saturated solution, the vapor tension drops from *d* to *g*. The latter value represents the vapor pressure of mixtures of the hydrate with the anhydrous salt. If the salt can form various hydrates, the vapor tension of the system water-salt at constant temperature is represented by a diagram such as that shown in Figure 10.[1]

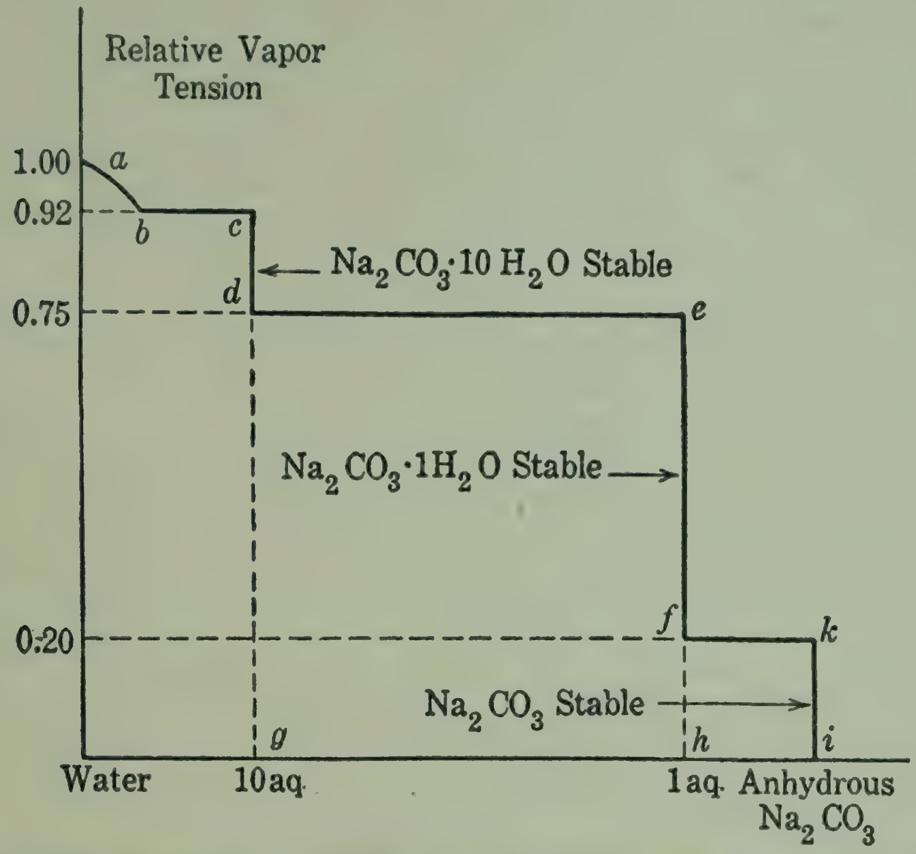


FIG. 10. Vapor pressure of water in the system water-sodium carbonate.

This diagram represents the system water-sodium carbonate. Ordinary crystallized sodium carbonate consists of the decahydrate; in addition there exists a monohydrate and, of course, the anhydrous form. At point *b* the solution is saturated with $Na_2CO_3 \cdot 10\,H_2O$. The vapor pressure remains constant up to *c*, corresponding to the pure decahydrate. The constant vapor pressure of mixtures of $Na_2CO_3 \cdot 10\,H_2O$ with $Na_2CO_3 \cdot H_2O$ is represented by *de*, and that of mixtures of the monohydrate with the anhydrous salt by *fk*. With the aid of diagrams such as the above we can easily predict what will happen when anhydrous salts or salt hydrates are exposed to the atmosphere. Atmospheric air contains varying amounts of water vapor, depending upon climatological and meteorological conditions. During rainy weather the air is nearly saturated with water vapor, and the aqueous tension at various temperatures corresponds approximately to the data given on p. 127. As a rule the atmosphere is not saturated with water vapor. It is customary to express the *relative humidity* or the *degree of humidity* by the ratio of the prevailing water-vapor tension to that of air saturated with water at the same temperature. By multiplying this relative humidity by 100, the *percentage of relative humidity* is obtained. Suppose, for example, that the water-vapor tension of the atmosphere at 25° is 11.88 mm. Then since air saturated with water vapor at 25° has a vapor tension of 23.76 mm., the relative humidity is equal to $\frac{11.88}{23.76} = 0.50$, and the percentage humidity is 50. The humidity of the air is determined with a hygrometer or psychrometer. It should be realized that the humidity of the air in laboratories changes considerably with the season. In winter in cold climates, when the buildings are heated, the laboratory air is nearly always extremely dry, relative humidities as low as 0.10 to 0.20 often being observed. In the summer, however, the humidity of the laboratory air is close to that of the atmosphere and in damp weather can reach values close to saturation.

---

[1] From N. Schoorl, *Commentaar op de Nederlandsche Pharmacopee*, p. 37, Vÿfde Uitgave, Utrecht, A. Oosthoek, 1927.

Let us consider what happens when various types of salts or salt hydrates are exposed to air of different humidities. Figure 8 represents the vapor tension of the system water-sodium nitrate. Point d represents the vapor tension; the ratio of the vapor pressure of the solution to that of pure water at the same temperature is 0.74 at 25°. If the relative humidity of the air is larger than 0.74, say f, the salt will attract water, and form a saturated solution. After all the salt has dissolved, it will continue to absorb water until the composition of the solution (g) is such that it has the same relative vapor pressure as the atmosphere. This phenomenon is called *deliquescence* and occurs only when the humidity of the air is greater than the vapor tension of the saturated salt solution. If the relative humidity of the air is less than 0.74, solid sodium nitrate will remain unchanged. When we are dealing with a salt hydrate, the latter may, depending upon the conditions, remain unchanged or deliquesce or give off water. Sodium bromide, for example, can exist as dihydrate and as anhydrous salt. The saturated solution of the hydrate has a relative vapor pressure of 0.57 at 25°. Therefore it will deliquesce when the relative humidity of the air is greater than 0.57. The dihydrate itself has a relative vapor pressure of 0.36 at 25° and therefore will give off water when the humidity of the air becomes smaller than 0.36. This process is called *efflorescence*. Sodium bromide dihydrate is stable only when kept at relative humidities between 0.36 and 0.57 (at 25°). From Figure 10 it is seen that $Na_2CO_3 \cdot 10\ H_2O$ is stable at relative humidities between 0.92 and 0.75. Therefore it effloresces very easily with the formation of the monohydrate. The latter effloresces in turn when the relative humidity is less than 0.20. Or, starting from the other side we may say that anhydrous sodium carbonate is not hygroscopic unless the humidity of the air is greater than 0.20. In the latter case it will be transformed into the monohydrate, and therefore no liquid phase is formed.

The phenomena described are of great analytical importance:

1. Analysis of salts which deliquesce very easily. A saturated solution of potassium hydroxide in water has a relative vapor tension of 0.05 at 25°. Therefore the solid will deliquesce very rapidly when exposed to air. A sample for analysis should be weighed in a well-closed weighing bottle; if the weighing were made in a vessel open to the air, the sample would continuously increase in weight.

2. For volumetric analysis it is of great importance to have pure salts or salt hydrates available as primary standard substances and to keep them in an unchanged state. Borax, for example, having the composition $Na_2B_4O_7 \cdot 10\ H_2O$, is an excellent primary standard for the standardization of acids. A saturated solution of borax has a relative water-vapor

tension of 0.99 at 20°; therefore deliquescence is not to be feared under any conditions. The relative vapor tension of borax is 0.39 at 20°, when it is in equilibrium with $Na_2B_4O_7 \cdot 5\ H_2O$. Therefore if borax is exposed to air of relative humidity less than 0.39, it will effloresce to the pentahydrate. The latter is stable only at relative humidities between 0.39 and 0.25; if the relative humidity becomes less than 0.25, the pentahydrate will effloresce to the anhydrous salt. It has been the experience of the authors that substances kept in ordinary glass-stoppered bottles are usually not protected from atmospheric influences. With different types of bottles it was found that pure borax always effloresced during the winter season. However, it can be kept unchanged in bottles which are hermetically closed. It is much safer, however, to preserve a sample of the pure borax in an atmosphere in which it is stable, i.e., at a relative humidity between 0.99 and 0.39 (20°). This can be done by placing the sample in a desiccator in which the humidity is kept constant by a suitable mixture. We have seen, for example, that a mixture of sodium bromide dihydrate and its aqueous solution has a constant humidity at a given temperature (0.59 at 20°, 0.57 at 25°). Therefore, if we place some anhydrous sodium bromide in a desiccator and add enough water to transform it into the dihydrate, and in addition a little more to assure the presence of a saturated solution of the latter, the atmosphere in this desiccator will have a relative humidity of 0.57 (25°), and borax will be quite stable. It is still better to keep the borax at a relative humidity of 0.70. Such arrangements, by which the humidity in a certain space is kept constant, are called *hygrostats* by N. Schoorl. After nearly all of the solid sodium bromide has dissolved by taking on water, the dish in which it has been placed in the hygrostat can be heated on a steam bath to recover the original product.

The use of hygrostats is also of great practical importance in the preparation of pure salt hydrates. The latter can be purified by recrystallization from water, but the final product always contains occluded mother liquor. The latter is removed by Schoorl's method, which consists of efflorescing the salt to a lower hydrate or the anhydrous form by placing it over a dehydrating agent (see p. 163). By this process the crystals usually break down into an extremely fine powder, and consequently the mother liquor is removed. The product obtained is then placed in a hygrostat of the proper aqueous tension to take up hydrate water and not used until the salt has reached constant weight. Pure oxalic acid dihydrate, borax, and sodium thiosulfate are prepared and kept in the above way. It may be mentioned here that the use of a salt or a salt hydrate with its saturated solution is more advantageous than the use of a solid mixture of a salt with its lower hydrate or its anhydrous form. In the former case equilibrium is attained much more rapidly than in the latter.

In the following tables the relative aqueous-vapor pressures of various mixtures of solids, and of solids with their saturated solutions are given. The data are taken from N. Schoorl.[1]

---

[1] N. Schoorl, *Chemisch Jaarboekje der Nederlandsche Chemische Vereeniging*, p. 171, Deel II, 15th ed., 1930.

TABLE XXV. RELATIVE VAPOR TENSIONS OF MIXTURES OF ANHYDROUS SOLIDS AND THEIR HYDRATES OR OF TWO HYDRATES

MIXTURE	RELATIVE VAPOR PRESSURES AT VARIOUS TEMPERATURES				
	10° C.	15°	20°	25°	30°
$MgCl_2 + MgCl_2 \cdot 2\,H_2O$			0.0005		
$KOH + KOH \cdot 1\,H_2O$					0.02
$CaCl_2 + CaCl_2 \cdot 1\,H_2O$			0.015		
$CaCl_2 \cdot 1\,H_2O + CaCl_2 \cdot 2\,H_2O$		0.05			
$NaOH + NaOH \cdot 1\,H_2O$			0.03		
$K_2CO_3 + K_2CO_3 \cdot 2\,H_2O$				0.05	
$NaI + NaI \cdot 2\,H_2O$		0.12	0.13	0.14	0.15
$CaCl_2 \cdot 2\,H_2O + CaCl_2 \cdot 6\,H_2O$	0.21	0.21	0.22	0.22	0.23
$Na_2HPO_4 + Na_2HPO_4 \cdot 2\,H_2O$		0.27	0.28	0.29	
$NaBr + NaBr \cdot 2\,H_2O$	0.30	0.32	0.34	0.36	0.38
$Na_2HPO_4 \cdot 2\,H_2O + Na_2HPO_4 \cdot 7\,H_2O$	0.50	0.53	0.56	0.59	0.62
$Na_2CO_3 \cdot 1\,H_2O + Na_2CO_3 \cdot 10\,H_2O$	0.66	0.69	0.72	0.76	
$Na_2HPO_4 \cdot 7\,H_2O + Na_2HPO_4 \cdot 12\,H_2O$	0.65	0.70	0.75	0.81	
$Na_2SO_4 + Na_2SO_4 \cdot 10\,H_2O$	0.69	0.72	0.76	0.80	

TABLE XXVI. RELATIVE VAPOR TENSIONS OF MIXTURES OF SOLIDS WITH THEIR SATURATED SOLUTIONS IN WATER

SATURATED SOLUTION OF	RELATIVE VAPOR PRESSURES AT VARIOUS TEMPERATURES				
	10°	15°	20°	25°	30°
P_2O_5			0		
KOH			0.05		
$NaOH$			0.06		
$CaBr_2 \cdot 6\,H_2O$	0.23	0.21	0.19	0.17	0.15
$CaCl_2 \cdot 6\,H_2O$	0.38	0.35	0.32	0.29	0.26
$K_2CO_3 \cdot 2\,H_2O$			0.44	0.45	
$Ca(NO_3)_2 \cdot 4\,H_2O$	0.65	0.60	0.55	0.50	0.45
$NaBr \cdot 2\,H_2O$	0.63	0.61	0.59	0.57	0.55
NH_4NO_3	0.69	0.66	0.63	0.60	0.57
$NaCl$	0.75	0.75	0.75	0.75	0.75
$NaNO_3$	0.77	0.76	0.75	0.74	0.73
KCl			0.86	0.85	0.85
$Na_2SO_4 \cdot 10\,H_2O$		0.95	0.90	0.85	0.78
$Na_2CO_3 \cdot 10\,H_2O$			0.91	0.89	0.87
KNO_3			0.95	0.94	0.94

Adsorbed and sorbed water.

Solids exposed to the atmosphere quite generally adsorb some water vapor on their surfaces. The relation between the amount adsorbed and the water-vapor tension is given by the so-called adsorption isotherm, an example of which is presented in Figure 11. The adsorption is relatively large at small pressures and changes rapidly in this region with the vapor pressure. Quite generally the adsorption decreases with increasing temperature.

Ordinarily when considering the adsorption of water by solids, we speak of *surface condensation*, meaning by this that we are not dealing with a simple gas adsorption but with a condensation of adsorbed vapor. In order to get such a liquid layer, it is necessary that the surface be wetted by the adsorbed substance.

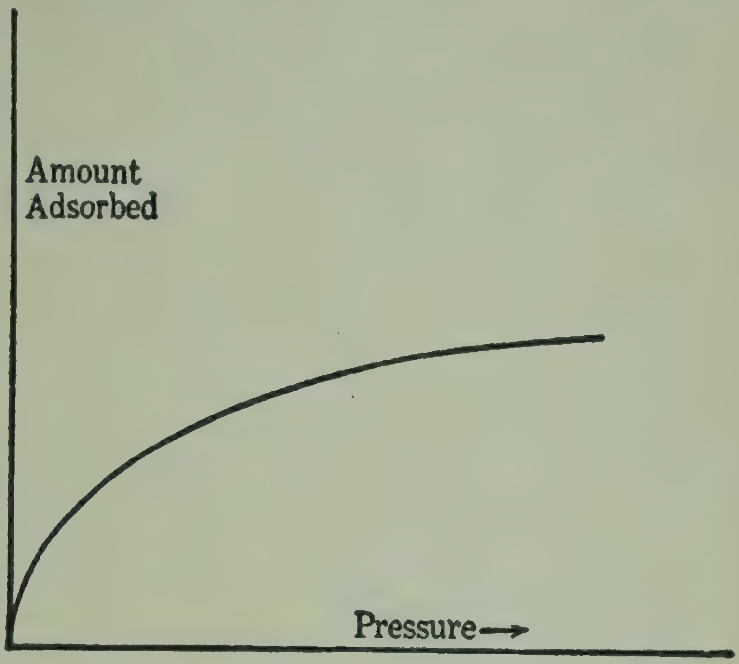


FIG. 11. Adsorption isotherm (gas-solid).

In precise analyses (atomic-weight determinations) the adsorption taking place on the surface of the containers in which weighings are being made can become significant. Warburg and Ihmori[1] determined the condensation on various surfaces in air partly saturated with water vapor. Some results are given in Table XXVII. The second column gives the thickness of the water layer in mm., the third, the weight of the condensed water per dm.² of surface. The data reported indicate the order of magnitude of the water condensation.

TABLE XXVII. SURFACE CONDENSATION OF WATER ACCORDING TO IHMORI[2]

KIND OF SURFACE	THICKNESS OF WATER LAYER	WEIGHT OF ADSORPTION LAYER OF WATER PER DM.²
	mm.	mg.
Platinum	10^{-5}	0.1
Washed Jena glass	10^{-5}	0.1
Unwashed Jena glass	3.3×10^{-5}	0.33
Ordinary glass	$10\text{–}100 \times 10^{-5}$	1–10
Agate	10^{-3}	10

If glass is heated to temperatures above 150°, it is difficultly wetted by water; and if left in contact with water vapor, it is only slowly wetted again. From the above it is clear that slight deviations in analytical results may occur if weighings are made in large glass containers. If the latter are heated and then cooled in a desiccator, the weight will gradually increase when they are placed on the balance. The final equilibrium is reached much more rapidly from the wet side than from the dry. Therefore it is recommendable to wipe a glass container (e.g., calcium chloride tube in water determinations) with a damp cloth and let it stand for about 15 minutes in the balance case before weighing. It should be realized that the weight of the glass container remains the same only when the humidity and the temperature of the atmosphere remain unchanged.

---

[1] E. Warburg and T. Ihmori, Wied. Ann. *27*, 481 (1886); Ihmori, *ibid.* *31*, 1006 (1887); Cohnstaedt, Physik. Z. *10*, 643 (1909); Parks, Phil. Mag. (6) *5*, 517 (1903).

[2] R. Strömberg, Avhandl. Akad. Stockholm III Ser. *6*, No. 2 (1929), gives data on the adsorption of water by fused silica, gold, and platinum at different humidities. As an example we cite his data for platinum (mg. p. dm.²): r.h. 20, 0.019; r.h. 40, 0.034; r.h. 60, 0.063; r.h. 80, 0.134; r.h. 100, 0.378.

Finely divided substances attract water from the atmosphere and hold it on their surfaces. Equilibrium is usually attained within 5 to 10 minutes. The water adsorbed is usually called *water of hygroscopicity;* its amount increases with increasing surface area and increasing humidity of the air. Therefore such substances, after cooling in a desiccator, should be weighed in well-closed weighing bottles, for otherwise they will attract water very rapidly again.

Many substances of colloidal character have a huge internal surface development and can adsorb very large amounts of water. In such cases equilibrium is reached very slowly; instead of adsorption we speak of a *sorption* process. The water taken up by the material is sometimes called *water of imbibition.* Silica gel, hydrous oxides, and various organic colloids such as cellulose, starch, agar, and proteins show such a behavior.[1] In the air-dry state they may contain more than 20 to 30 per cent of water and still retain the appearance of perfectly dry powders. The water content of such substances changes considerably with varying humidities of the atmosphere. Potato starch, for example, may contain about 10 per cent of water at a relative humidity of 0.20, and 21 per cent of water at a relative humidity of 0.70. Thus, if such substances are kept in ordinary bottles which are not hermetically closed, their water content may change greatly with the seasons. The change in the moisture content with varying water-vapor tension of the atmosphere is usually given by an S-shaped curve. Figure 12,[2] representing the water content of silica gel at various humidities, shows this clearly. The top curve, giving the molar ratios of sorbed water to SiO_2 after 750 hours' exposure to various vapor tensions, shows the S-shape plainly. It is also seen that equilibrium is reached very slowly; even after 10 days it was not attained.

In Figure 13 the water contents of gelatine, potato starch, and cellulose, respectively, are given [3] for various relative humidities. As a rule it is not a very simple matter to determine the water content of such materials. On drying at temperatures of 100° to 115°, the water is given off slowly; moreover it is impossible to remove the last traces of water, since the surrounding air has a certain humidity, and the sorption at very low aqueous-vapor pressures is still relatively large. Heating at much higher temperatures (180°–200°) involves the danger of decomposition, especially when dealing with organic materials. In such cases it is necessary to dry in a vacuum oven at 70°–100° and remove the water given off or to dry in a current of air which has been deprived of its water vapor. Great precaution must be taken in the final weighings, since the dried material is extremely hygroscopic and adsorbs water very rapidly when exposed to the air. Therefore the weighings should be made in well-closed containers.

---

[1] Pioneer work in this field has been done by J. M. van Bemmelen, Z. anorg. allgem. Chem. *5*, 466 (1894); *13*, 233 (1897); *18*, 14, 98 (1898); *30*, 265 (1902); J. M. van Bemmelen and E. A. Klobbie, J. prakt. Chem. *46*, 497 (1892); Rec. trav. chim. *7*, 37 (1888); Z. anorg. allgem. Chem. *49*, 125 (1906).

[2] I. M. Kolthoff and V. A. Stenger, J. Phys. Chem. *38*, 250 (1934).

[3] From N. Schoorl, *loc. cit.*, p. 120.

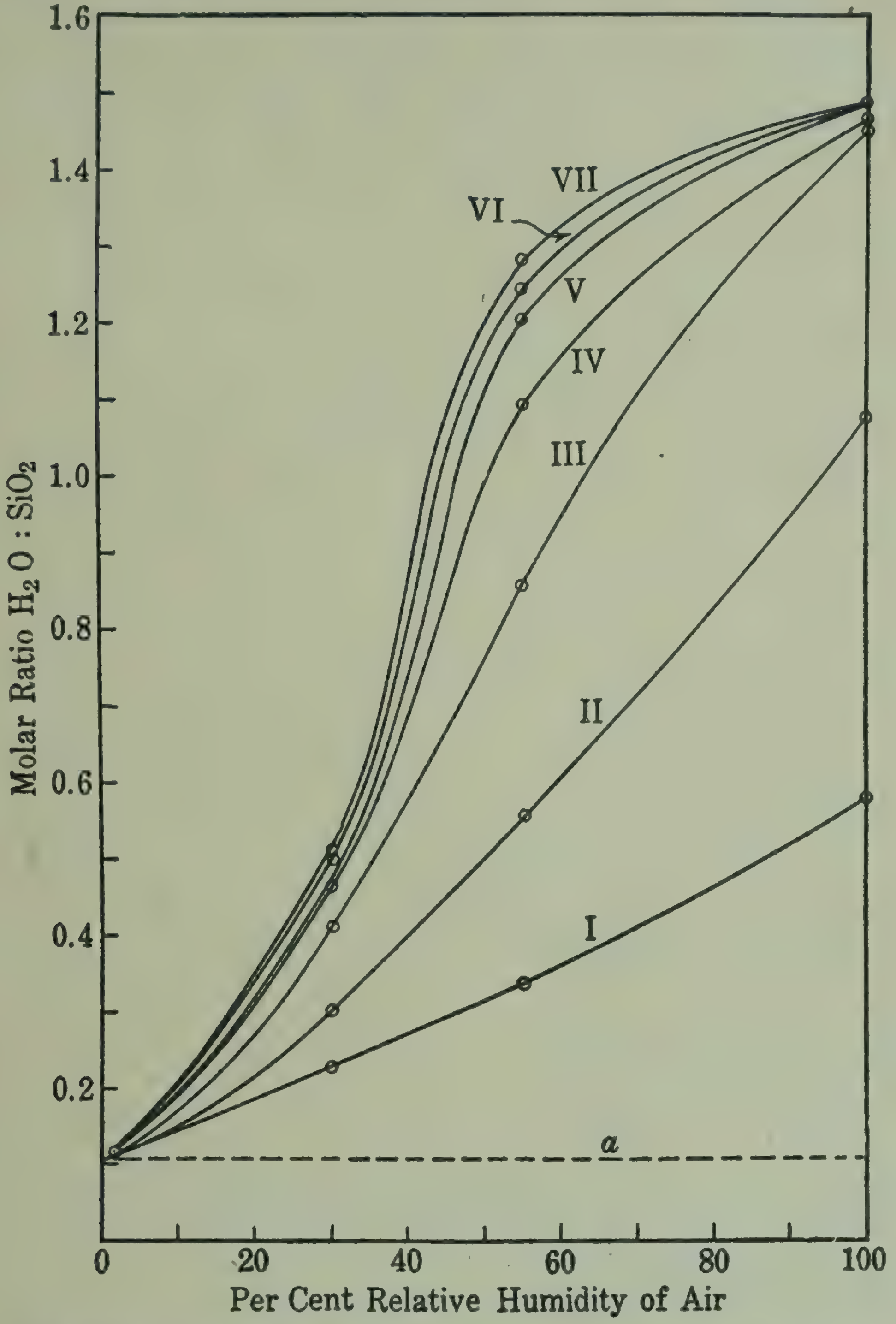


FIG. 12. Adsorption of water by silica gel. The dotted line *a* represents the initial ratio of H_2O to SiO_2, and the curves I to VII give the ratio after 4, 10, 24, 48, 96, 192, and 750 hours' exposure, respectively, of the gel to atmospheres of the relative humidity indicated.

The hygroscopic properties of cellulose are of analytical interest, since filter paper consists of this material. If a substance were collected on filter paper, dried at 100°–120°, and weighed after cooling, the dried paper would attract water very readily (see curve for cellulose in Fig. 13).

Since the sintered glass, porous porcelain, or Gooch filter crucibles (see p. 185) do not show such behavior to any appreciable extent, they are always used for such purposes.

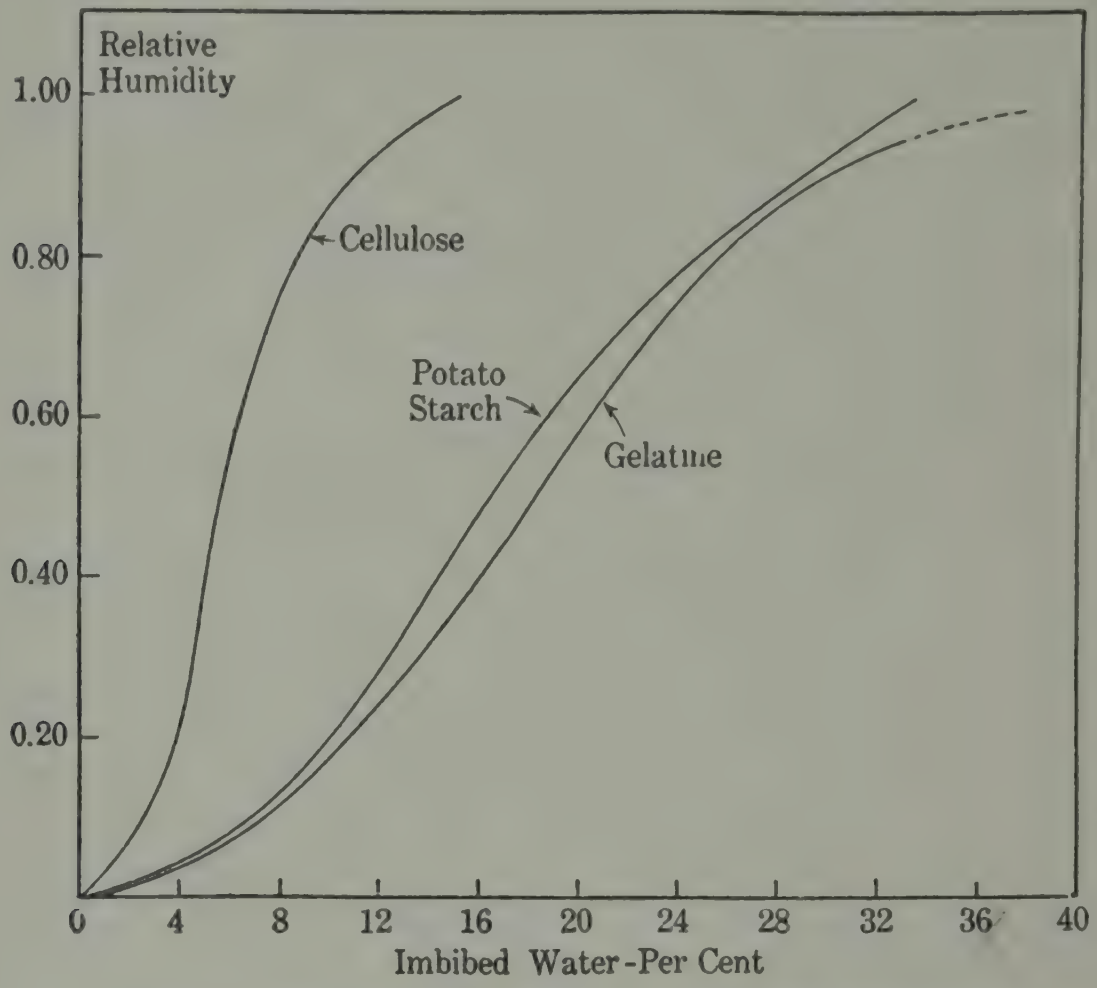


FIG. 13. Imbibition of water by colloidal substances.

The states of water in solids.

1. *Nonessential water.*

(1) *Water of hygroscopicity.* In a previous paragraph we saw that finely divided substances adsorb water on their surfaces. The amount of hygroscopic water increases with increasing surface area. As a rule it is extremely small after ignition of a precipitate, at least if the latter does not combine chemically with the water. If the precipitate is not ignited, the amount of hygroscopic water can be relatively large, since it is adsorbed at both the external and internal surfaces (see p. 105). It is found, for example, that calcium oxalate monohydrate formed under analytical conditions is very hygroscopic after drying at 100°–105° and can take up 1 per cent of water. If such a dried precipitate is weighed unprotected in the air, its weight increases rapidly. It should be understood that adsorbed water is not always quantitatively removed by heating at 100°–130°. The processes of adsorption and desorption of water are reversible.

(2) *Occluded water.* Precipitates, and solids in general, contain occluded water in the interior of the material. Occluded water is not removed by heating at 100° but disappears continuously at much higher temperatures. Most crystals separated from aqueous medium contain occluded

water. In most macroscopic crystals cavities filled with mother liquor may be seen with the aid of the microscope (Fig. 14). But even if these cavities are not microscopically visible, water is usually present in amicroscopic cavities or in an adsorbed state at the internal isolated surface. On heating such crystals containing cavities, the former burst open at higher temperatures (*decrepitation*). In the coprecipitation of foreign ions the latter are adsorbed during the growth of the precipitate in a more or less hydrated state.

In addition water may be distributed homogeneously throughout the solid. Such cases occur, for example, with natural glasses, which may contain several per cent of water.

Summarizing then, occluded water may be present in cavities containing mother liquor, in the adsorbed state at the internal surface, and finally in solid solution.

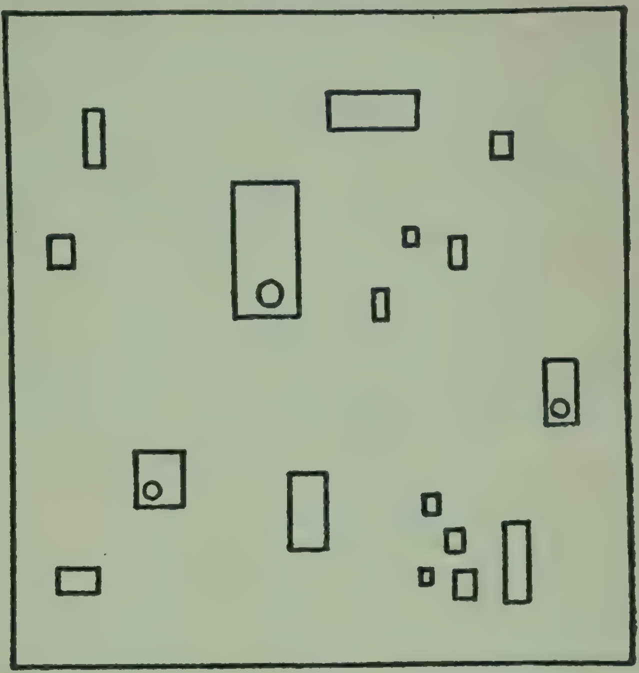


FIG. 14. Liquid and gas inclusions in potassium chloride crystal (× 100).

(3) *Water of imbibition.*[1] In a previous paragraph it was mentioned that sorbed water in organic lyophilic colloids is removed slowly and incompletely by heating at temperatures from 100° to 150°. By working in a vacuum at higher temperatures, it usually escapes completely; in this way it is often possible to determine sorbed water and occluded water separately.

Hillebrand[2] in a discussion of the condition of hydrogen in minerals, mineral aggregates, and mineral powders gives the following classification of nonessential hydrogen:

> "*Non-essential hydrogen* — its presence not necessary for characterization of the mineral. (Considered as water or other compounds.)
>
> I. *In liquid solution*, specially in deliquescent powders, also in amorphous material, including undercooled liquids.

---

[1] Water of imbibition can be taken up in different ways:

1. The water is sorbed without changing the lattice of the original material.
   (a) The original lattice may contain vacant spaces easily accessible to water and other vapors. Water may condense in these spaces. This occurs, for example, with substances of a zeolitic nature.
   (b) The crystallites in lyophilic organic colloids adsorb water at their surfaces, this process being accompanied by a swelling (starch, agar).
2. The sorbed water changes the lattice of the material.
   (a) Water penetrates into the lattice, giving rise to a continuous increase of the distance between the planes of a layer lattice, and therefore to a swelling. The case occurs, for example, with graphitic acid. (J. R. Katz and J. C. Derksen, Rec. trav. chim. *53*, 652 [1934].)
   (b) A definite hydrate is formed.

[2] W. F. Hillebrand, *Analysis of Silicate and Carbonate Rocks*, p. 64, U. S. Geol. Survey Bull. 700 (1919). W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*, p. 676, John Wiley and Sons, New York, 1929.

II. *Held by surface forces.*
  a. Absorbed on surfaces in films of molecular thickness [usually monomolecular thickness].
    1. On walls of cavities within grains of aggregates.
    2. On exteriors of grains.
  b. Held by capillarity, in liquid form.
    1. In colloids with mesh structure.
    2. In definite openings within grains of aggregates.
    3. In spaces between separate grains.

III. *Included.*
  a. As liquid droplets in cavities.
  b. As included grains of minerals belonging to one of the above listed classes."

2. *Essential water.*

(1) *Water of crystallization.* Various precipitates crystallize as hydrates which are stable in the air between certain limits of humidity. This, for example, is the case with $MgNH_4PO_4 \cdot 6\,H_2O$ and $CaC_2O_4 \cdot H_2O$, which can be weighed as such.

Water of crystallization in salts can be determined as a rule by indirect analysis, i.e., by determining the weight before and after heating. If the salt decomposes on heating, it is often possible to find a temperature range over which the water of crystallization is completely removed, without decomposition of the salt (Chapter XVI). If the water cannot be removed without decomposing the solid, a direct water determination must be resorted to.

(2) *Water of constitution.* The water is not present as such but in the form of hydroxyl or hydrogen chemically bound in the compound. On heating, decomposition takes place with formation of water, which may be called water of constitution.

EXAMPLES: On heating Na_2HPO_4 or $KHSO_4$, water of constitution is expelled:

$$2\,Na_2HPO_4 \rightarrow Na_4P_2O_7 + H_2O$$
$$2\,KHSO_4 \rightarrow K_2S_2O_7 + H_2O.$$

In these cases the hydrogen is removed as water. On heating of calcium and magnesium hydroxides, hydroxyl is also removed as water:

$$Ca(OH)_2 \rightarrow CaO + H_2O.$$

Hillebrand (*loc. cit.*) gives the following classification of essential hydrogen in minerals:

"*Essential hydrogen* — present in regular atomic arrangement in molecular or crystal structure.

I. Present in definite, stoichiometric proportions:
  a. As hydrogen — called acidic by analogy to behavior in solutions.
  b. As hydroxyl — the hydrogen called basic, again by analogy.
  c. As water — especially water of crystallization.

II. Not present in stoichiometric proportions with reference to the substances as a whole, but present, in one of the above forms, in one or more of the constituents of mixed crystals, including isomorphous mixtures."

When dealing with substances, such as minerals, containing various types of essential and nonessential water, an exact determination of each may be difficult. Nevertheless, considerable information may be obtained by appropriate analytical procedures and application of physico-chemical methods. For a more detailed discussion the student is referred to the excellent treatment of Hillebrand (*loc. cit.*).

In connection with the above, a few words may be said with regard to sampling of solids for analysis. On grinding of mineral powders, the surface is increased and hence the water adsorption from the atmosphere. They may retain appreciable amounts of this adsorbed water, even in excess of 1 per cent, after heating to temperatures far above 100°. Moreover, it should be realized that the water content of the sample changes with the humidity of the air, if it is not kept in tightly closed containers.

Although more water is adsorbed by the ground material than the coarse powder, water of crystallization may be expelled from solids by long-continued grinding.

PROBLEMS

1. How may a sample of partially effloresced sodium thiosulfate pentahydrate be transformed entirely into the pentahydrate? The pentahydrate is stable between relative aqueous-vapor pressures of 0.23 and 0.69 at 20°.

2. Na_2HPO_4 is kept at the following relative vapor tensions: 0.25, 0.40, 0.65, 0.75 respectively at 25°. What is the composition of the solid after equilibrium has been reached in each case? How could the water of hydration and the water of constitution be determined separately?

CHAPTER X

THEORY OF ELECTROANALYSIS

Reactions at electrodes.

In an ordinary gravimetric analysis the substance to be determined is precipitated from solution by the addition of an excess of a chemical reagent. In an electroanalysis the ion to be determined is deposited on a suitable electrode by the passage of an electric current; the process is called an *electrolysis.*

When pieces of platinum foil, connected to the poles of a battery, are immersed in an aqueous solution of copper chloride, metallic copper is deposited on the piece of foil connected to the negative pole of the battery, and chlorine gas is formed at the other foil. These pieces of foil are called *electrodes;* the one attached to the positive pole of the battery is called the *anode,* and that joined to the negative pole the *cathode.* (See Fig. 15, in which the arrows indicate the direction of the current, i.e., direction of flow of positive charges.)

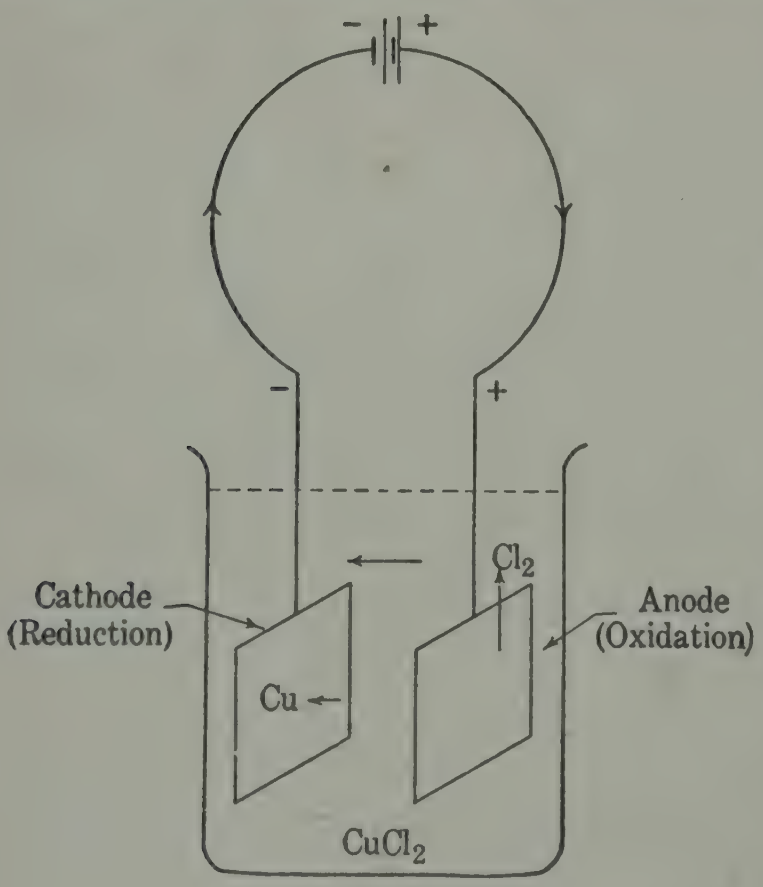


FIG. 15

During electrolysis the copper separates as metal on the cathode, the chlorine as the free element at the anode. This corresponds to a *reduction at the cathode* and an *oxidation at the anode.* Electrochemically, oxidation and reduction are defined by the *electron transfer* from one substance (ion or uncharged molecule) to another. *A substance is oxidized when it loses electrons,* and *it is reduced when it takes on electrons.* The relation is represented by the following equation:

$$\text{Ox} + n\,e \rightleftarrows \text{Red}.$$

Ox denotes the oxidized state, and Red the reduced state resulting from the addition of n electrons (e). The reduction which takes place when a metal is electrodeposited at the cathode can be represented by the general equation:

$$M^{n+} + n\,e \rightleftarrows M,$$

n being the valence of the ion (e.g., for Bi, $n = 3$; Ni, $n = 2$; Ag, $n = 1$). When a metal can exist in more than one state of oxidation, it is often possible under proper conditions to reduce it at the cathode from a higher state of oxidation to a lower state, without separating the metal itself:

$$\mathrm{Fe^{+++}} + e \rightleftarrows \mathrm{Fe^{++}}$$
$$\mathrm{Sn^{++++}} + 2\,e \rightleftarrows \mathrm{Sn^{++}}.$$

On changing the conditions, the reduced forms can be further reduced to the metallic state:

$$\mathrm{Fe^{++}} + 2\,e \rightleftarrows \mathrm{Fe}$$
$$\mathrm{Sn^{++}} + 2\,e \rightleftarrows \mathrm{Sn}.$$

At the anode an oxidation takes place:

$$\mathrm{Red} \rightleftarrows \mathrm{Ox} + n\,e.$$

The anode therefore behaves as an absorber of electrons and the cathode as a supplier of electrons. Not all anions can be oxidized to the corresponding discharged state. This occurs in the electrolysis of halides at an unattackable anode:

$$\mathrm{Cl^-} \rightleftarrows \tfrac{1}{2}\,\mathrm{Cl_2} + e$$
$$\mathrm{I^-} \rightleftarrows \tfrac{1}{2}\,\mathrm{I_2} + e.$$

Hydroxyl ions, on discharge, yield oxygen and water:

$$2\,\mathrm{OH^-} \rightleftarrows \tfrac{1}{2}\,\mathrm{O_2} + \mathrm{H_2O} + 2\,e.$$

The latter reaction also takes place during the electrolysis of solutions containing sulfates, phosphates, etc. In aqueous medium sulfate ions are *not* discharged according to the equations:

$$\mathrm{SO_4^=} \rightleftarrows \mathrm{SO_4} + 2\,e,$$
$$\mathrm{SO_4} + \mathrm{H_2O} \rightarrow \mathrm{H_2SO_4} + \tfrac{1}{2}\,\mathrm{O_2},$$

because it is easier to discharge the hydroxyl ions, even if the concentration of the latter is extremely small, as in acid medium.

Oxidation at the anode does not necessarily lead to the formation of uncharged compounds. Depending upon the conditions, any kind of oxidation may take place. Suppose, for example, that a solution of copper sulfate is electrolyzed, a copper cathode and a copper anode being used. At the cathode the following reduction takes place:

$$Cu^{++} + 2\,e \rightarrow Cu.$$

At the anode the reverse reaction occurs, metallic copper going into solution.

If a halide is electrolyzed using a silver anode, the following reaction takes place:

$$Ag \rightarrow Ag^{+} + e.$$

The silver ions react with the halide ions to form insoluble silver halide on the anode. The total reaction taking place may then be written as follows:

$$Cl^{-} + Ag \rightarrow AgCl + e.$$

Use can be made of this reaction in the electroanalysis of chloride, bromide, and iodide.[1]

Metal ions can be oxidized at the anode from a lower state of oxidation to a higher one, for example:

$$Fe^{++} \rightarrow Fe^{+++} + e.$$

Use is made of this fact in the electroanalysis of some metals which under the proper conditions can be separated at the anode in the form of higher oxides, for example, in the determination of lead, manganese, molybdenum, and uranium:

$$Pb^{++} \rightarrow Pb^{++++} + 2\,e.$$

The plumbic ions are not stable in aqueous medium and react with water to form lead dioxide:

$$Pb^{++++} + 2\,H_2O \rightarrow PbO_2 + 4\,H^{+}.$$

A similar equation can be written for the electrodeposition of manganese in the form of manganese dioxide.

Laws of electrolysis.

The brilliant researches of the English scientist Michael Faraday (1791–1867) resulted in the discovery of the relation which exists between the quantity of electricity which passes through a solution and the quantity of matter which separates at the electrodes.

The first law of Faraday states: *The quantities of substances set free at the electrodes are directly proportional to the quantity of electricity which passes through the solution.* Thus the quantity of a metal liberated at the cathode during the passage of ten coulombs of electricity through a solution of the metal salt is five times that which is deposited when two coulombs pass through the solution.

---

[1] J. H. Hildebrand, J. Am. Chem. Soc. *29*, 447 (1907); T. P. McCutcheon J. Am Chem. Soc. *29*, 1445 (1907).

The second law states: *The same quantity of electricity sets free the same number of equivalents of any substance at the electrodes.* This law implies that the passage of the same quantity of electricity through solutions of copper chloride, silver sulfate, and hydrobromic acid sets free quantities of copper, chlorine, silver, oxygen, hydrogen, and bromine that are proportional to the equivalent weights, or in a ratio of:

$$\frac{63.57}{2} : \frac{35.457}{1} : \frac{107.88}{1} : \frac{16.000}{2} : \frac{1.0078}{1} : \frac{79.916}{1}.$$

If in a certain case two ions are discharged simultaneously by a quantity of electricity sufficient to discharge one gram-equivalent of a substance, then the sum of the quantities of the two substances discharged simultaneously will be equal to one gram-equivalent.

The relation between the three fundamental quantities, current, resistance, and electromotive force, is expressed by *Ohm's law*, which states: *The current I is directly proportional to the electromotive force E and inversely proportional to the resistance R:*

$$I = \frac{E}{R} \text{ or } E = IR.$$

Electrical units.

The unit of current is called the *ampere* in honor of the French physicist and chemist A. M. Ampere (1775–1836). One ampere is that current which deposits 1.11800 mg. of silver (or 0.3296 mg. of copper, etc.) from a solution in one second.[1] Current is measured by means of an instrument called an *ammeter*.

The unit *quantity* of electricity is called the *coulomb* in honor of the French physicist C. A. Coulomb (1736–1806). The coulomb is defined as that quantity of electricity which flows through a given cross section of a conductor in one second when the current is one ampere. One coulomb, therefore, will deposit 1.11800 mg. of silver.

The unit of electrical resistance is the *ohm*, so called after the German physicist G. S. Ohm (1787–1854), who discovered the relation between *I*, *E*, and *R*. One ohm is equal to the resistance at 0° of a column of mercury 106.3 cm. in length and 1 sq. mm. in cross section.

---

[1] The above definition is that of the "International Ampere." The "absolute" ampere is defined as follows:

If, in a conductor, 6.25×10^{18} electrons flow through a certain cross section in one second, the current is equal to one ampere. The quantity of electricity associated with the electron is 4.774×10^{-10} e.s.u. (electrostatic units). The "International Ampere" and the "absolute ampere" are practically identical.

The unit of electromotive force (and potential difference) is called the *volt* after the Italian physicist Count A. Volta (1745–1827). One volt is the electromotive force required to maintain a current of 1 ampere through a conductor having a resistance of 1 ohm. Electromotive force (E.M.F.) is measured by means of a *voltmeter*.

The number of grams of an element set free by the passage of 1 coulomb of electricity (or 1 ampere-second) is called the *electrochemical equivalent* of the element. According to Faraday's laws, electrochemical equivalents are proportional to chemical equivalents. The electrochemical equivalent of silver is, as we have seen, 0.001118 g. It is of interest to calculate the amount of electricity required to liberate one equivalent of an element. From Faraday's first law we learn that this amount is found by dividing the gram-equivalent weight by the electrochemical equivalent. Thus in the case of silver: $\frac{107.88}{0.001118} = 96494$, or approximately 96500 coulombs. This quantity of electricity is called the *faraday* (*F*). In accordance with the second law of electrolysis, the passage of one faraday of electricity will liberate one gram equivalent of some substance at each electrode.

Faraday's laws of electrolysis are among the most exact laws of physical science; they hold under all conditions, independent of the concentration of the electrolyte, of the temperature, and of the solvent used.

Electrode potentials and E.M.F. of cells.

The various ions are not discharged with the same ease. A lower electromotive force will suffice to discharge, for example, silver ions than copper ions at the same concentration, and the latter are reduced more easily than zinc ions. Iodide is more easily discharged than chloride. The electromotive force required for the discharge of an ion is closely related to the so-called *normal potential* of the particular system, as will now be explained.

If a metal is placed in a solution containing ions of the metal (for example, silver in a silver nitrate solution), a potential difference *E* is established between the metal and the solution, the value of which is given by Nernst's equation (1889):[1]

---

[1] We omit the derivation of this fundamental equation since it may be found developed in any elementary textbook of physical chemistry.

Electrode reaction: $M \rightleftarrows M^{n+} + n\,e$

$$E = \text{const.} + \frac{RT}{nF}\, ln\, C_{\text{ion}}$$

in which R is the gas constant, T the absolute temperature, F the faraday, n the number of electrons taking part in the reaction, ln the natural logarithm, and C_{ion} the concentration of the metal ions in the solution.[1] By introducing the known values for R and F and changing from natural to common logarithms by multiplying by 2.3026, the above equation can be written:

$$E = \text{const.} + \frac{0.0001983\,T}{n} \log_{10} C_{\text{ion}}.$$

At a temperature of 30°, $T = 303$, and we have

$$E = \text{const.} + \frac{0.060}{n} \log_{10} C_{\text{ion}} \quad (30^\circ) \quad \text{or}$$

$$E = E_o + \frac{0.060}{n} \log C_{\text{ion}}.$$

For any particular electrode there is a simple relation between E and the ion concentration C. When C is equal to one, E is equal to E_o. This particular value, E_o, is called the *normal* or *standard potential* of the system. The single potential difference between an electrode and a solution (electrode potential) [2] cannot be measured with any degree of accuracy; therefore the potential is always related to the potential of another electrode which is taken as the standard. There is an international agreement to relate all data to the so-called normal hydrogen electrode, the potential of which is *arbitrarily* set equal to zero.

In Table XXVIII the normal potentials of various metals are given with respect to the normal hydrogen electrode. Let us consider the significance of the figures given in the table and take as an example the silver-silver ion electrode. The normal potential of this electrode is given as + 0.81 volt. This means that the silver electrode in a solution with a silver-ion concentration (activity) of one has a potential of + 0.81 volt as measured against the normal hydrogen electrode. A hydrogen electrode

---

[1] To be strictly accurate, ion activities should be written here instead of ion concentrations.

[2] E denotes the potential difference between electrode and solution and is called the potential of the electrode. Naturally the difference in potential between solution and electrode is $-E$ and is called the electrode electromotive force (E.M.F.). For a discussion of the relation between the potential and the E.M.F. of an electrode see F. H. MacDougall, *Physical Chemistry*, The Macmillan Co., New York, 1936.

TABLE XXVIII. NORMAL POTENTIALS OF METALS AND SOME METALLOIDS

ELECTRODE REACTION	E_0 (Volts)	ELECTRODE REACTION	E_0 (Volts)
$Li \rightleftharpoons Li^+ + e$	− 3.02	$I^- \rightleftharpoons \frac{1}{2} I_2 + e$	+ 0.53
$K \rightleftharpoons K^+ + e$	− 2.92	$Br^- \rightleftharpoons \frac{1}{2} Br_2 + e$	+ 1.07
$Na \rightleftharpoons Na^+ + e$	− 2.71	$Cl^- \rightleftharpoons \frac{1}{2} Cl_2 + e$	+ 1.36
$Ba \rightleftharpoons Ba^{++} + 2e$	− 2.8		
$Mg \rightleftharpoons Mg^{++} + 2e$	− 2.34	$H_2O \rightleftharpoons \frac{1}{2} O_2 + 2H^+ + 2e$	+ 1.23
$Zn \rightleftharpoons Zn^{++} + 2e$	− 0.76		
$Fe \rightleftharpoons Fe^{++} + 2e$	− 0.44	$S^= \rightleftharpoons S + 2e$	− 0.55
$Cd \rightleftharpoons Cd^{++} + 2e$	− 0.40		
$Ni \rightleftharpoons Ni^{++} + 2e$	− 0.25		
$Co \rightleftharpoons Co^{++} + 2e$	− 0.28		
$Sn \rightleftharpoons Sn^{++} + 2e$	− 0.14		
$Pb \rightleftharpoons Pb^{++} + 2e$	− 0.13		
$\frac{1}{2} H_2 \rightleftharpoons H^+ + e$	0.00		
$Bi \rightleftharpoons Bi^{+++} + 3e$	+ 0.2		
$Sb \rightleftharpoons Sb^{+++} + 3e$	+ 0.2		
$As \rightleftharpoons As^{+++} + 3e$	+ 0.3		
$Cu \rightleftharpoons Cu^{++} + 2e$	+ 0.345		
$2Hg \rightleftharpoons Hg_2^{++} + 2e$	+ 0.80		
$Ag \rightleftharpoons Ag^+ + e$	+ 0.81		
$Pd \rightleftharpoons Pd^{++} + 2e$	+ 0.82		
$Au \rightleftharpoons Au^+ + e$	+ 1.5		

consists of a noble metal like platinum, which is coated with a layer of the noble metal, say platinum black, and which is saturated with hydrogen gas. The potential difference between this electrode and a solution which has a hydrogen concentration (activity) of one and which is saturated with hydrogen under a pressure of one atmosphere is called the potential of the normal hydrogen electrode, which is arbitrarily set equal to zero. According to the above terminology the normal potential of silver is equal to the E.M.F. (electromotive force) of a cell consisting of the two half-cells, normal silver electrode, designated by $Ag \mid 1\,M\,Ag^+$, and the normal hydrogen electrode, designated by $Pt \mid H_2$ 1 atm. $1\,M\,H^+$. Thus the normal potential of silver is equal to the E.M.F. of the cell:

$$- Pt \mid H_2 \text{ 1 atm. } 1\,M\,H^+ \parallel 1\,M\,Ag^+ \mid Ag +,$$

in which the silver electrode is the positive and the half-cell at the left the negative electrode. The symbol $\parallel$ indicates that a liquid-junction potential is eliminated.

With the aid of the values in the table one can calculate the E.M.F. of cells consisting of two different metal electrodes immersed in solutions containing the respective metals. Consider, for example, the cell

$$- \text{Zn} \mid M\ \text{ZnSO}_4 \parallel M\ \text{CuSO}_4 \mid \text{Cu} +$$

(Cu is the positive and Zn the negative electrode), which is the familiar Daniell element. The potential of the copper electrode is + 0.345 volt, that of the zinc electrode − 0.76 volt. The potential *difference* between the two electrodes, which is equal to the E.M.F. of the cell, then is + 0.345 − (− 0.76) = 1.105 volts (cf. Fig. 16).

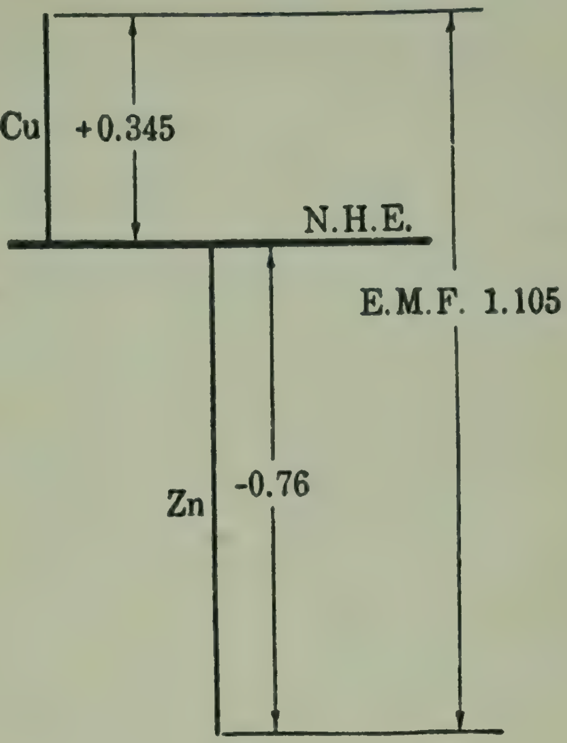


FIG. 16

If we reduce the copper sulfate concentration from 1 molar to 0.01 molar, leaving the zinc concentration unchanged, the potential of the copper electrode becomes:

$$E = 0.345 + \frac{0.060}{2} \log 0.01 = 0.285 \text{ volt}$$

and E.M.F. = 0.285 − (− 0.76) = 1.045 volts.

The cell $- \text{Zn} \mid M\ \text{ZnSO}_4 \parallel M\ \text{CdSO}_4 \mid \text{Cd} +$

has an E.M.F. = − 0.40 − (− 0.76) = 0.36 volt (cf. Fig. 17).

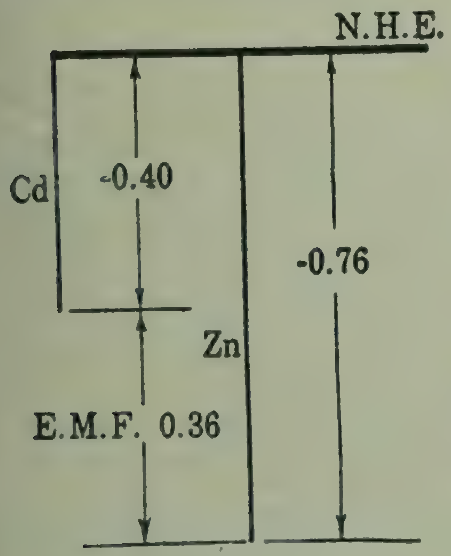


FIG. 17

The Nernst equation can be extended to any *reversible* oxidation-reduction reaction which takes place at an electrode:

$$\text{Ox} + n\,e \rightleftarrows \text{Red}.$$

The potential of the non-attackable electrode at which such a reaction takes place is called the *oxidation* potential and is determined by the general expression:

$$E_{\text{Ox}} = \frac{RT}{nF}\, ln \frac{[\text{Ox}]}{[\text{Red}]} + \text{Const.}$$

[Ox] represents the concentration of the oxidized form, and [Red] that of the reduced form. At 30° we find again:

$$E_{\text{Ox}} = E_o + \frac{0.060}{n} \log \frac{[\text{Ox}]}{[\text{Red}]}. \quad (30°)$$

This expression is seen to be identical with that for a metal electrode, if we realize that in the latter case the concentration of the reduced form, the metal itself, which is insoluble, becomes constant.

For the potential of the chlorine electrode we find then that

$$\tfrac{1}{2}\,Cl_2 + e \rightleftarrows Cl^-$$

$$E = E_o + 0.060 \log \frac{\sqrt{[Cl_2]}}{[Cl^-]}. \qquad (30°)$$

Similarly, the potential of the oxygen electrode is

$$\tfrac{1}{2}\,O_2 + H_2O + 2\,e \rightleftarrows 2\,OH^-$$

$$E = E'_o + \frac{0.060}{2} \log \frac{\sqrt{[O_2]}}{[OH^-]^2}.$$

Since

$$[OH^-] = \frac{K_w}{[H^+]},$$

it is found that

$$E = E'_o + \frac{0.060}{2} \log \frac{\sqrt{[O_2]}}{K_w^2} + \frac{0.060}{2} \log [H^+]^2.$$

Oxygen gas is very slightly soluble in water, and therefore $[O_2]$ is constant as a rule. Since K_w is constant at a given temperature, the expression $\frac{0.060}{2} \log \frac{\sqrt{[O_2]}}{K_w^2}$ becomes constant. We find then

$$E = E_o + \frac{0.060}{2} \log [H^+]^2 = E_o + 0.060 \log [H^+]$$

in which E_o again is a constant but has a value different from E'_o in the previous equation.

The oxygen potential in a solution 1 *N* with respect to hydrogen ions is equal to 1.23 volts. If oxygen is set free by electrolysis on a polished platinum electrode, the potential as a rule is higher than 1.23 (as a result of the so-called overvoltage, which is discussed in a subsequent section), and is equal to approximately 1.70 volts. Thus if we would measure the E.M.F. of the cell

$$-\ (Pt)H_2 \mid M\ HClO_4 \parallel M\ HClO_4 \mid O_2(Pt)\ +,$$

when it was operating spontaneously (furnishing current), we would find an E.M.F. equal to 1.23 volts, since the potential of the normal hydrogen electrode is arbitrarily set equal to zero. When the cell operates spontaneously, the following reactions occur at the electrodes:

Oxygen electrode: $\tfrac{1}{2}\,O_2 + 2\,e + H_2O \rightarrow 2\,OH^-$
Hydrogen electrode: $H_2 \rightarrow 2\,H^+ + 2\,e$
Net cell reaction: $\tfrac{1}{2}\,O_2 + H_2 \rightarrow H_2O$

The net reaction in the cell is obtained by summation of the two equations. In the left half-cell hydrogen gas goes into solution to form hydro-

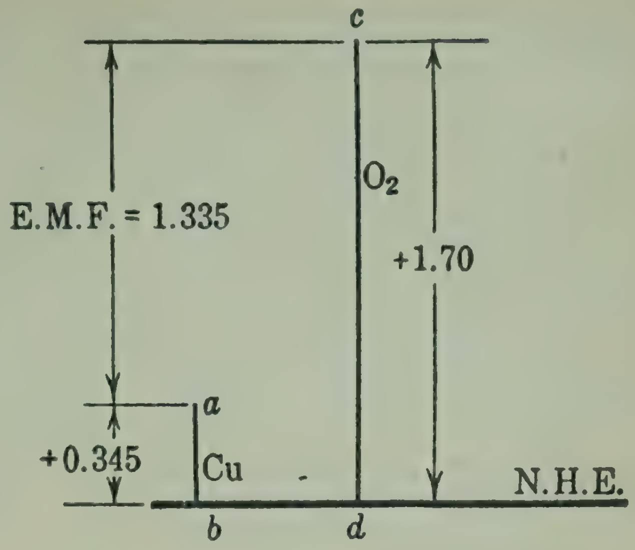


FIG. 18

gen ions, and in the right half-cell oxygen gas goes into solution to form hydroxyl ions. However, if we would reverse the cell reaction, by opposing an external E.M.F., we would find that an applied E.M.F. of 1.70 volts would be required to discharge hydrogen on the cathode and oxygen on the anode. It has been found by experiment that the additional E.M.F. (1.70 − 1.23) required for electrolysis is due chiefly to oxygen overvoltage at the anode, the overvoltage of hydrogen on smooth platinum being small. In electrolysis, the cell

$$- \mathrm{Cu} \mid M\ \mathrm{Cu(ClO_4)_2} \parallel M\ \mathrm{HClO_4} \mid \mathrm{O_2(Pt)} +$$

will require an E.M.F. of 1.70 − 0.345 = 1.355 volts (see Fig. 18), and the cell

$$- \mathrm{Zn} \mid M\ \mathrm{Zn(ClO_4)_2} \parallel M\ \mathrm{HClO_4} \mid \mathrm{O_2(Pt)} +$$

will require an E.M.F. of

$$1.70 - (-0.76) = 2.46 \text{ volts (Fig. 19).}$$

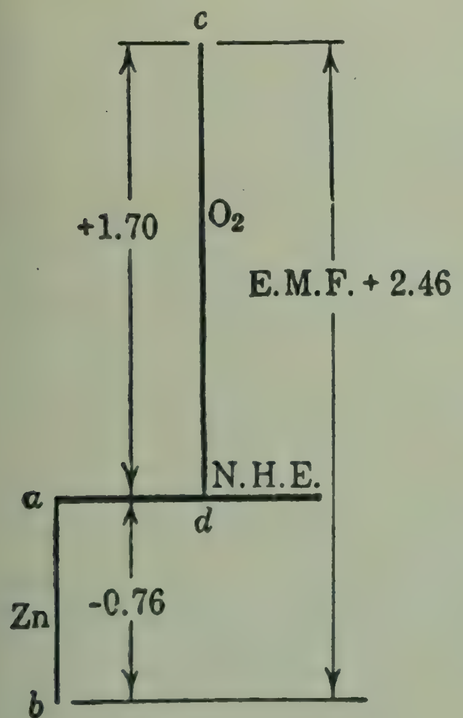
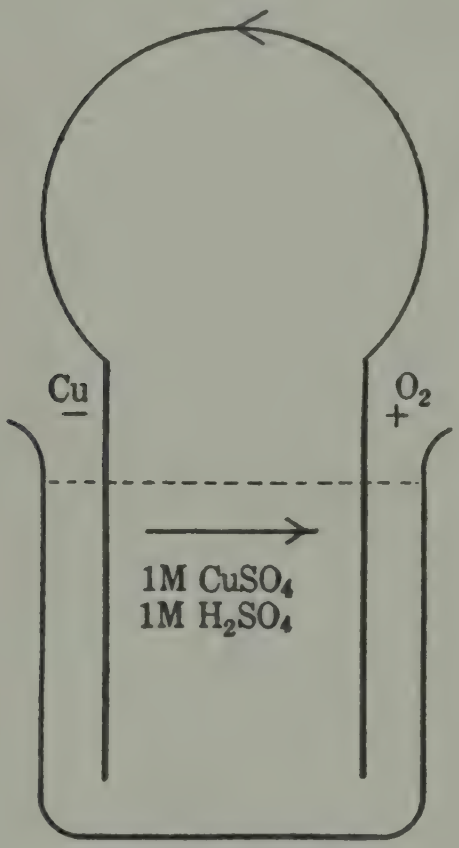


FIG. 19

Decomposition voltage. If smooth (i.e., bright) platinum electrodes are dipped into a molar solution of copper sulfate in molar sulfuric acid, and are connected through an ammeter with a battery having an electromotive force less than 1.35 volts, a current will at first flow through the circuit. Its strength, as shown by the ammeter, decreases rapidly and after a very short time becomes virtually equal to zero. If now the battery is removed and the circuit completed by means of a wire, the ammeter will deflect in the opposite direction. After what has been said in the previous paragraph, the above phenomenon is easily understood. If we set up the following cell:

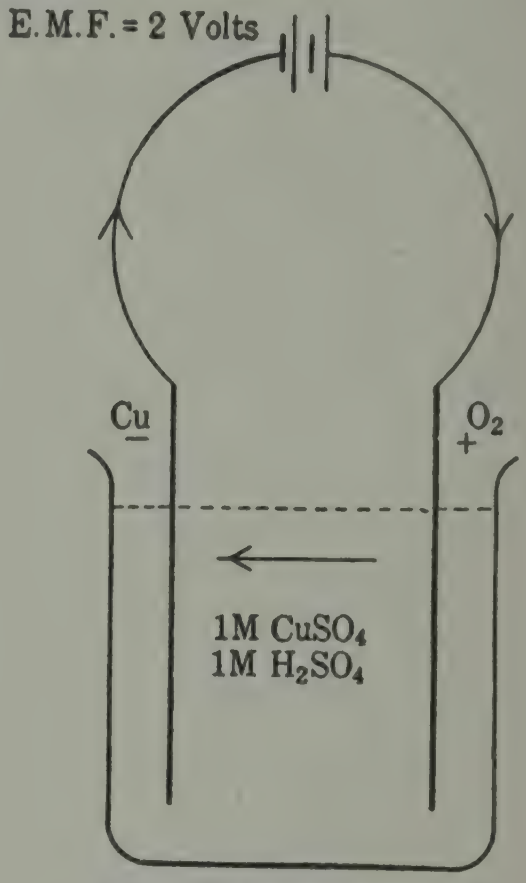
$$- \mathrm{Cu} \mid M\ \mathrm{CuSO_4} \parallel M\ \mathrm{H_2SO_4} \mid \mathrm{O_2(Pt)} +$$

and connect the two electrodes by a wire, a current will flow through the solution from the copper electrode to the oxygen electrode (cf. Fig. 20), and the cell operates spontaneously. In the electrolysis, the anode (oxygen electrode) is connected with the positive pole of the battery, and the cathode with the negative pole; hence the current flows through the solution from the oxygen electrode to the copper electrode, as indicated by the arrows in Fig. 21. It is clear that the E.M.F. of the cell counteracts the applied E.M.F.; there is developed what is called a *back* E.M.F. The cell $Cu \mid M\ CuSO_4 \parallel M\ H_2SO_4 \mid O_2(Pt)$ has an E.M.F. of 1.355 volts; therefore no measurable electrolysis occurs until the applied E.M.F. becomes greater than this value.



E.M.F. = 1.355 Volts

FIG. 20



Back E.M.F. = 1.355 Volts

FIG. 21

The exact understanding of the back E.M.F. and the decomposition voltage is not simple and may cause the student some difficulty. To aid in the understanding of the concept of back E.M.F., we may describe the phenomena in the following way. When the cell in Figure 20 operates spontaneously, electrons flow from the negative copper electrode to the positive oxygen electrode, where they react with oxygen to form hydroxyl ions. Hence when the cell operates spontaneously, a *reduction occurs at the positive* oxygen electrode. The flow of electrons from copper to the oxygen electrode is identical with the flow of positive electricity (positive current) from the oxygen to the copper electrode, resulting in an oxidation of copper to copper ions.

$$\begin{array}{ll} \text{Oxygen electrode:} & \tfrac{1}{2}\,O_2 + H_2O + 2\,e \rightarrow 2\,OH^- \\ \text{Copper electrode:} & \qquad\qquad\quad Cu \rightarrow Cu^{++} + 2\,e \\ \hline \text{Net cell reaction:} & \tfrac{1}{2}\,O_2 + Cu + H_2O \rightarrow 2\,OH^- + Cu^{++} \end{array}$$

The driving force of this net cell reaction is 1.355 volts. In the electrolysis we wish the reactions to occur in the opposite direction; in other words, we wish to reduce the copper ions at the copper electrode and to oxidize hydroxyl ions to oxygen at the oxygen electrode.

Oxygen electrode: $2\,OH^- \rightarrow \frac{1}{2}\,O_2 + H_2O + 2\,e$
Copper electrode: $Cu^{++} + 2\,e \rightarrow Cu$
Net electrolysis reaction: $2\,OH^- + Cu^{++} \rightarrow \frac{1}{2}\,O_2 + Cu + H_2O$

In order to have the net electrolysis reaction take place, we must overcome the driving force of the net cell reaction (1.355 volts), which tends to make the reaction run in the opposite direction. In other words, in order to have the electrolysis reaction take place, we must apply an E.M.F. which is greater than 1.355 volts. *The lowest external electromotive force that must be applied in order to bring about the continuous separation of the cation and the anion* (or oxygen) *is called the decomposition voltage of the electrolyte.*

The decomposition voltage is determined experimentally by plotting the current as indicated by an ammeter against increasing external electromotive force. Practically no current goes through the solution until the decomposition voltage has been reached, and then with further increase in the E.M.F. the current increases very rapidly, as indicated in Fig. 22.

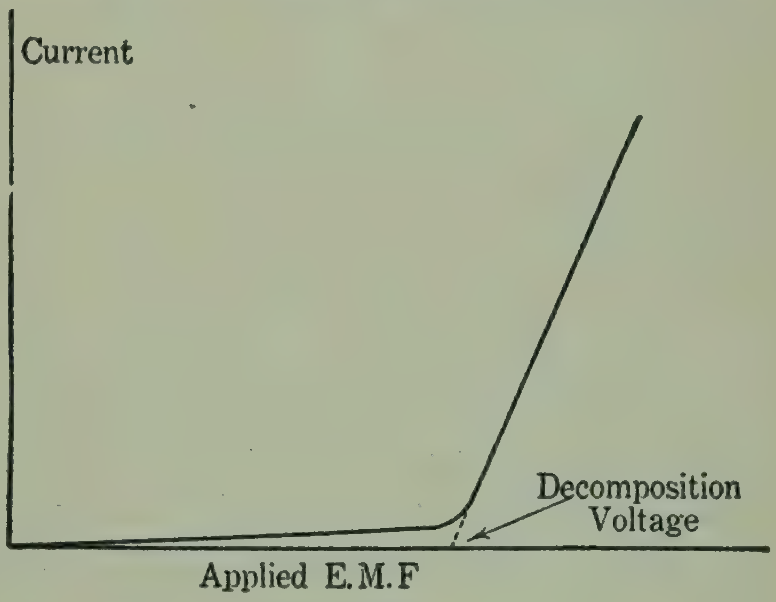


FIG. 22

The current is determined by Ohm's law,

$$E_a = E_d + IR,$$

in which E_a is the applied E.M.F., E_d the "back E.M.F." or the decomposition voltage, and R the resistance of the system. The current I is then:

$$I = \frac{E_a - E_d}{R}.$$

The decomposition voltage has been determined by Le Blanc[1] in 0.5 to 1 molar solutions of various salts using bright platinum electrodes. Theoretically, the decomposition voltage is equal to the algebraic difference of the potentials of the cathode and of the anode, which in turn are determined by the particular ions and the ion concentrations. Actually the values found are usually different, because of the phenomenon of *overvoltage* at the electrodes. (See next paragraph.) However, the values determined by Le Blanc have practical significance and are therefore given in Table XXIX.

---

[1] M. Le Blanc, Z. physik. Chem. *8*, 299 (1891); *12*, 333 (1893).

TABLE XXIX. DECOMPOSITION VOLTAGES ACCORDING TO LE BLANC

ELECTROLYTE	CONCENTRATION (MOLARITY)	DECOMPOSITION VOLTAGE
$ZnSO_4$	0.5	2.35
$ZnBr_2$	0.5	1.80
$CdSO_4$	0.5	2.03
$CdCl_2$	0.5	1.88
$Cd(NO_3)_2$	0.5	1.98
$NiSO_4$	0.5	2.09
$NiCl_2$	0.5	1.85
$CoSO_4$	0.5	1.92
$CoCl_2$	0.5	1.78
H_2SO_4	0.5	1.67
$HClO_4$	1	1.65
HNO_3	1	1.69
HCl	1	1.31
$Pb(NO_3)_2$	0.5	1.52
$AgNO_3$	1	0.70

Overvoltage.

It is found that the decomposition voltage of an electrolyte varies with the nature of the electrodes used for the electrolysis. Thus, a higher voltage is required to decompose a solution of sulfuric acid between a platinum anode and a copper cathode than between two platinum electrodes. This excess voltage, over the algebraic difference of the reversible electrode potentials, is known as *overvoltage.* It may occur at the anode as well as at the cathode. Thus the decomposition voltage E_d is equal to

$$E_d = e_a - e_c + e_{o.a.} - e_{o.c.},$$

in which $e_a - e_c$ represents the algebraic difference of the potentials at the anode and cathode, $e_{o.a.}$ the overvoltage at the anode, and $e_{o.c.}$ the overvoltage at the cathode.

The overvoltage in the separation of metals is, as a rule, very small and may be neglected from the practical viewpoint. The overvoltages in the liberation of hydrogen at the cathode and of oxygen at the anode may become fairly large; the hydrogen overvoltage especially is of great practical importance.

The overvoltage at either the anode or cathode is a function of the following variables:[1]

---

[1] H. A. Fales and F. Kenny, *Inorganic Quantitative Analysis*, 2d ed., p. 472, The Appleton-Century Co., New York. Fales again refers to A. J. Allmand and H. J. T. Ellingham, *The Principles of Applied Electrochemistry*, 2d ed., p. 73, Longmans, Green & Co., New York, 1931.

"1. The kind of metal that is used for an electrode, whether platinum, iron, copper, etc.

"2. The physical state in which the ion comes out at the electrode when it is discharged; if it appears as a metal, the overvoltage is small, if as a gas, however, the overvoltage is relatively very great.

"3. The current density employed:[1] increase in current density means increase in overvoltage; for current densities from 0.00005 amp./cm.^{2} up to 0.01 amp./cm.^{2} the increase in overvoltage is very rapid, beyond current densities of 0.01 amp./cm.^{2} the increase in overvoltage still continues, but far less rapidly.

"4. The concentration gradient existing around the electrodes; as this increases, the overvoltage rises.

"5. The temperature of the solution; increased temperature decreases the overvoltage because it helps in keeping down the concentration gradient at an electrode by virtue of the convection currents which it produces in the solution and by virtue of the increased mobility which it imparts to the ions. To this the beneficial effect of effective stirring of the solution may be added."

Overvoltage of hydrogen. For the overvoltage of hydrogen from acid solution, Fales (*loc. cit.*, p. 472) gives the following figures for various cathode materials at various current densities, when dilute sulfuric acid (up to 1 molar) is used as the electrolyte and the electrolysis is conducted at room temperature.

TABLE XXX. OVERVOLTAGE FOR HYDROGEN IN ACID SOLUTION

NATURE OF CATHODE	CURRENT DENSITY (AMPERES/CM.^{2})		
	0.00005	0.01	0.1
	Overvoltage (Volts)		
Smooth platinum	0.08	0.07	0.29
Platinized platinum	0.00	0.03	0.04
Gold	0.02	0.39	0.59
Mercury	0.57	1.04	1.07
Copper	0.19	0.58	0.85
Tin	0.40	1.08	1.22
Iron	0.17	0.56	0.82
Zinc	0.48	0.75	1.06

In alkaline medium the hydrogen overvoltage as a rule is somewhat larger (0.1 to 0.3 volt) than in acid medium.

The anodic overvoltage of oxygen in acid medium on smooth platinum is approximately 0.4 volt (current density 0.023 amp. per cm.^{2}). The anodic overvoltage in alkaline medium is about 1 volt greater than in acid medium.

---

[1] The current density (N.D.) is the current per unit area of electrode surface. It is usually expressed in amperes per square centimeter; in electroanalysis a larger unit, amperes per square decimeter, N.D.$_{100}$ is often used.

Platinum anodes are usually used in electroanalysis, since most other metal electrodes dissolve as a result of the reaction at the electrode.

Electroanalysis.

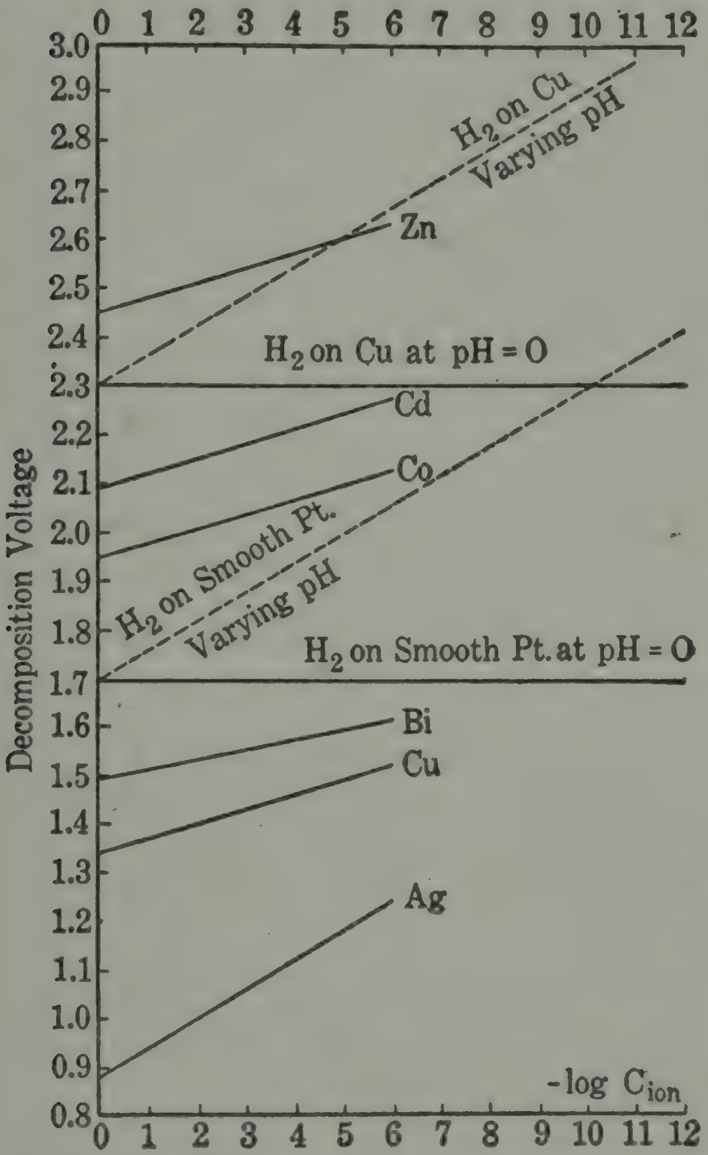


FIG. 23. Decomposition voltage of metals as sulfates in 1 *N* H_2SO_4.

In Figure 23 the decomposition voltages of various metal sulfates, as calculated from the normal potentials, are plotted as a function of the metal concentration in the solution. The abscissa gives the negative logarithm of the ion concentration; the value 0 corresponds to an ion concentration of 1 molar, the value 6 to a concentration of 10^{-6} molar, etc. From a quantitative viewpoint we may consider the electrodeposition to be complete when the ion concentration has decreased to a value of 10^{-6} molar. The change of the decomposition potential with the concentration is calculated with the aid of Nernst's equation (see p. 144).

The solid horizontal line at a voltage of 1.69 represents the decomposition voltage of hydrogen in 1 *N* sulfuric acid on smooth platinum; that at 2.3 volts, the same on copper. The dotted lines give the change of the decomposition voltage of sulfuric acid on smooth platinum and copper at various pH values. The latter are read on the scale at the top of the graph. A simple study of the figure teaches us many things which are of great practical importance.

Completeness of deposition of a metal. During an electrolysis the E.M.F. between the anode and the cathode is read on a voltmeter *V* (see Fig. 75, p. 420). Suppose now that we electrolyze an acid solution of copper sulfate and keep the voltage fairly constant between 1.9 and 2.1 volts. From the graph it is seen that the copper concentration in the solution has decreased to 10^{-6} molar at a voltage of 1.53. The copper concentration corresponding to a voltage of 2.0 volts is so small that it has hardly any practical significance.

A voltage of 1.35 corresponds to a copper-ion concentration at the cathode of 1 molar. Therefore, according to Nernst's equation, a voltage of 2.0 volts corresponds to:

$$(1.35 - 2.0) = -0.65 = \frac{0.060}{2} \log [\mathrm{Cu}^{++}]$$
$$-\log [\mathrm{Cu}^{++}] = 21.7$$
$$[\mathrm{Cu}^{++}] = 2 \times 10^{-22}.$$

The hydrogen overvoltage on copper is approximately 0.6 volt (current density 0.01 amp./cm.^{2}); therefore hydrogen is not evolved until the voltage is raised to about 2.3 volts. Therefore a copper solution can be electroanalyzed in acid medium without any interference from hydrogen evolution. In addition it is seen that when the copper concentration has reached the value of approximately 10^{-22} molar the electrolysis automatically comes to a stop:

$$E_a = E_d + IR.$$

When E_a becomes equal to E_d, I becomes equal to zero. Thus in the electroanalysis of a copper sulfate solution one could use a lead accumulator, having an E.M.F. of about 2.1 volts, as a source of current and let the apparatus stand overnight at room temperature. The next day all the copper would be separated, and practically no current is wasted. What has been said for copper naturally holds qualitatively for metals such as silver, bismuth, etc.

If a zinc sulfate solution is electrolyzed in acid medium, hydrogen will be evolved before the zinc is set free, even if a copper-plated platinum cathode is used. (Zinc should never be plated on pure platinum, since it forms an alloy with this metal which is not completely soluble in acid and the platinum is eventually spoiled.)

In order to electroanalyze a zinc solution, one can resort to the following modifications:

1. Decrease the hydrogen-ion concentration. Suppose that we are working in the presence of an acetate-acetic acid buffer having a hydrogen-ion concentration equal to 10^{-6}. The decomposition voltage of the acid is then raised according to Nernst's equation by $\frac{0.060}{1} \log 10^6 = 0.36$ volt. If a copper-plated platinum electrode is used as a cathode, the decomposition voltage of the acid is raised from 2.3 to approximately 2.7 volts (see Fig. 23), which is higher

than the value required to set free the zinc. If the hydrogen-ion concentration is further decreased by addition of sodium hydroxide, zinc hydroxide will precipitate and then dissolve as zincate in an excess of the base. If ammonia is used as the base, the zinc hydroxide will dissolve as an ammonio complex. In both cases most of the zinc is transformed into complex ions, and consequently a large decrease in the zinc-ion concentration, and therefore an increase in the decomposition voltage, results. The decomposition potential of hydrogen is raised as well, owing to the decrease of the hydrogen-ion concentration and to the increase of the overvoltage in alkaline medium. If all data (complex constant of the complex formed, and the overvoltage of hydrogen) are known, it is possible to calculate whether the electroanalysis can be carried out without interference from hydrogen liberation. These calculations are rather involved and not very exact.. Empirically, however, it has been found that various metals, such as zinc and nickel, can be advantageously electroanalyzed in ammoniacal medium or other complex solutions (cyanide).

2. Use a cathode at which the overvoltage of hydrogen is extremely great. An inspection of Table XXX shows that mercury is distinguished by its very high hydrogen overvoltage. W. Böttger[1] has made extensive investigations on the use of the mercury cathode in electroanalysis and has shown that it is an important tool in the quantitative electroanalysis of various metals which cannot be deposited on platinum on account of hydrogen evolution. Another advantage of mercury is that it forms amalgams with the separated metals. The amalgams may be considered as dilute solutions of the metals in mercury. When dissolved in mercury, metals have less tendency to go into solution than when present in their pure state (they behave more like noble metals). Therefore by using a mercury cathode in a solution of low hydrogen-ion concentration, it is even possible to determine the strongly electropositive alkali metals by electroanalysis.

Electroseparations.

In the preceding sections we have discussed the electroseparation of a single metal from hydrogen. The theory of the electroseparation of two different metals now becomes an easy matter. Let us take, for example, the case of a solution containing silver and copper. Figure 23 shows that at a voltage of 1.3 volts all the silver has been separated, whereas no copper has been deposited. Even if a higher voltage is applied, the silver will be set free quantitatively before the copper can come out. However, after the quantitative separation of the former, the copper will plate out unless the voltage is decreased or the electrolysis discontinued. The best way of proceeding is to measure the potential of the cathode (silver electrode) against some reference electrode during the analysis. The measured E.M.F. of this cell allows a calculation of the silver-ion concentration, and the electrolysis can be discontinued when the silver concentration has dropped to a low value. However, such a procedure requires a fairly complicated apparatus and great care and attention, and therefore it has not found widespread application.

---

[1] W. Böttger, Ber. *42*, 1824 (1909); T. P. McCutcheon, J. Am. Chem. Soc. *29*, 1445 (1907); H. S. Lukens and E. F. Smith, *ibid.* *29*, 1455 (1907); McCutcheon and Smith, *ibid.* *29*, 1460 (1907), especially W. Böttger, in *Physikalische Methoden der analytischen Chemie*, Vol. I, p. 137, Akademische Verlagsgesellschaft, Leipzig, 1936.

An inspection of Figure 23 and Table XXIX shows that various metals can be separated electrolytically with great ease (silver from copper, copper from zinc, etc.). However, when the normal potentials of the two metals are close together, the electroseparation becomes more involved. If a copper solution contains bismuth, antimony, or arsenic, the latter will deposit simultaneously with the copper. In these cases use can be made of the formation of complexes. Under these conditions the decomposition potentials of the metals forming complexes are raised, the values depending upon the particular metal and the stability constants of the complexes formed. Thus it may happen that a metal which in simple ionic solution is set free at a lower voltage than another metal may show the reverse behavior in a complex-forming solvent. In the following table are given the potentials (*e* cathode) of some metals in 0.1 molar solutions of their sulfates and also in the presence of various concentrations of potassium cyanide.

TABLE XXXI. POTENTIALS OF SOME METALS (e_c) IN SIMPLE AND ALKALI CYANIDE SOLUTIONS

METAL	e_c FOR 0.1 MOLAR SOLUTIONS OF METAL	CONCENTRATION OF EXCESS KCN PER 0.1 MOLE OF METAL CYANIDE		
		0.2 *M* e_c	0.4 *M* e_c	1 *M* e_c
Zn	− 0.79	− 1.03	− 1.18	− 1.23
Cd	− 0.43	− 0.71	− 0.87	− 0.90
Cu	+ 0.315	− 0.61	− 0.96	− 1.17

From this table it is seen that in simple solutions of copper and zinc the copper can easily be plated out quantitatively before zinc separates. In 1 molar potassium cyanide, however, the two decomposition potentials are close together, and the two metals are deposited simultaneously as an alloy (brass). It should be emphasized that the various data given in Figure 23 and Table XXIX are approximate only, since the values depend somewhat on experimental conditions. This is especially true for the metals nickel, cobalt, and iron, the potentials of which depend chiefly upon experimental conditions. However, the data demonstrate clearly the principles involved.

Influence of stirring and temperature. Character of the deposit.

Formerly it was customary to allow the electrolyte to stand quietly during electrolysis until the deposition was complete. The movement that naturally takes place within the solution under these circumstances is caused by ascending gas bubbles, convection, and diffusion. Nowadays a more rapid electroanalysis is generally preferred, and it is extremely important for the success of this method to prevent local depletion at the surface of the cathode of the ion to be deposited. In the case of stationary electrolytes, the decrease of the metal-ion concentration in the neighborhood of the cathode can only be counteracted by the slow process of diffusion and the slight stirring effect of the oxygen evolved at the anode. Consequently with stationary electrodes the concentration of the electrolyte very close to the cathode will be much smaller than in the bulk of the solution, and there then result an increase in the back E.M.F. and a decrease in the current. This effect is called *concentration polarization*, and it increases with increasing current density. In order to pass the desired current under such circumstances, a large E.M.F. would have to be applied, involving the risk of exceeding the hydrogen potential, with the consequent discharge of hydrogen ions. By adequate stirring, concentration polarization can be reduced until its effect is negligible. Various devices are used in practical work; rotating the cathode or the anode, or agitation by means of an independent stirrer all lead to good results. Increase of temperature increases the rate of diffusion in the electrolyte, although stirring is much more efficient than heating. Still, working at higher temperatures has some other advantages; it decreases the resistance of the electrolyte, consequently increasing the current and giving a denser and more adherent deposit. Therefore for many rapid determinations the temperature is maintained between 60° and 90°, and the solution is well stirred.

As far as the nature of the deposit is concerned, it is absolutely necessary that it shall adhere firmly to the cathode in order that the solution may be rinsed off at the end without loss of metal. For analytical purposes the deposit must be coherent, dense, and smooth. Such a deposit is finely crystalline, with a metallic luster. Flaky, spongy, and powdery deposits are less dense and less pure; they adhere only loosely to the cathode, and for these reasons they should be avoided. As a rule more satisfactory deposits are obtained when the metal is deposited from a solution in which it is present as a complex rather than as a simple ion. Increase of current density leads to a decrease in the grain size of the deposit; and if it is raised sufficiently, evolution of hydrogen may occur, owing to depletion of metal ions near the cathode. If an appreciable evolution of hydrogen occurs, the deposit will become broken up and irregular. In certain cases the addition of nitric acid to the electrolyzed solution is recommended. Nitric acid reacts with the hydrogen as it is formed at the cathode, functioning as a depolarizer:

$$NO_3^- + 10\,H^+ + 8\,e \rightarrow NH_4^+ + 3\,H_2O.$$

For analytical purposes the current densities that are employed are seldom in excess of 0.1 amp./cm.^{2} and usually are about 0.01 amp./cm.^{2} (stirring).

It should be emphasized that at the end of the electrolysis the current should not be shut off as long as the electrodes are in the solution. If the current is broken, the metallic deposit may slowly go back into solution.

Electrolysis without applied E.M.F. Internal electrolysis.

Electroanalysis by the spontaneous discharge of a galvanic cell in which the solution to be analyzed is the catholyte has been named "internal electrolysis."[1] In order to make the principle clear, let us consider the cell:

$$Pt \mid Cu^{++} \parallel Zn^{++} \mid Zn.$$

Although the potential of the platinum electrode in the copper-ion solution is badly defined, it will always be considerably more positive than that of the zinc electrode. Hence, when the cell is short-circuited, electrons flow from the zinc to the platinum electrode, giving rise to a reduction of the copper ions:

---

[1] H. J. S. Sand, Analyst *55*, 309 (1930); A. Schleicher, Z. anal. Chem. *83*, 127 (1931).

$$Cu^{++} + 2\,e \rightarrow Cu.$$

The platinum becomes coated with copper and behaves like a copper electrode which has a well-defined potential in the copper-ion solution. Simultaneously with the reduction of copper ions an oxidation of zinc occurs at the zinc electrode, the net cell reaction being:

$$Cu^{++} + Zn \rightarrow Cu + Zn^{++}.$$

Because of the great difference in potential between the zinc and copper electrodes, the separation of copper ions will be quantitative. This would be true even if the zinc-zinc sulfate were replaced, say, by cadmium-cadmium sulfate. The advantages, limitations, and specific applications of internal electrolysis have been discussed by Clarke, Wooten, and Luke [1] in a paper in which they describe the apparatus and the application of the method to the determination of copper and bismuth in an alloy, using a lead anode and a platinum-gauze cathode. For the determination of small quantities of mercury in the presence of copper and zinc by internal electrolysis, see Fife.[2]

PROBLEMS

1. During an electrolysis the applied E.M.F. as read on a voltmeter is equal to 3 volts. The back E.M.F. is equal to 1.5 volts, and the resistance of the system is 10 ohms. What is the current expressed in amperes? What is the current density at the cathode, if the latter has a surface area of 20 cm.^{2}? What is the current when the applied E.M.F. is reduced to 1.5 volts?

Ans. 0.15 amp.; 0.0075 amp. cm.^{2}; zero.

2. A current of 1 ampere is passed for 100 minutes through the following electrolyte solutions respectively: copper sulfate, silver nitrate, bismuth bromide, and sulfuric acid. What weights of Cu, Ag, Bi, Br_2, H_2, and O_2 are formed? What volumes of H_2 and O_2 are liberated (standard conditions)? (Faraday = 96500 coulombs.)

Ans. 1.977 g. Cu; 6.709 g. Ag; 4.332 g. Bi; 4.969 g. Br_2;
0.0627 g., 696 ml. H_2; 0.497 g., 348 ml. O_2.

3. Calculate the decomposition voltage of 0.01 N silver sulfate in 1 N sulfuric acid. The potential of the silver electrode in 0.01 N silver nitrate is + 0.69 volt, that of the oxygen electrode + 1.3 volts. The oxygen overvoltage is 0.4 volt. The silver is transformed into a complex and the silver-ion concentration reduced to 10^{-10} N. What is now the decomposition voltage? Assuming that the hydrogen-ion concentration remains 1 N and that the overvoltage of hydrogen on silver is equal to 0.5 volt (hence the potential of the cathode when hydrogen is discharged is − 0.5 volt), would there be any danger of hydrogen evolution before all the silver is deposited?

Ans. 1.01 volts; 1.49 volts. No. A total voltage of 2.2
would be required for H_2 evolution.

---

[1] B. L. Clarke, L. A. Wooten, and C. L. Luke, Ind. Eng. Chem., Anal. Ed. *8*, 411 (1936); see also J. J. Lurie and L. B. Ginsburg, *ibid.* *10*, 201 (1938).

[2] J. G. Fife, Analyst *63*, 650 (1938).

4. How much time is theoretically required for a current of 0.1 ampere to deposit all the silver from 100 ml. of 0.1 *N* silver nitrate solution?
Ans. 2.68 hours.

5. How could the current strength be increased during an electrolysis if the difference between the applied E.M.F. and back E.M.F., and the temperature are kept constant?

6. The back E.M.F. in the electrolysis of 0.1 *N* silver nitrate at the start is 0.76 volt. What is the value after the silver-ion concentration has been reduced to 0.001 *N*? *Ans.* 0.88 volt.

7. The potential of a dilute magnesium amalgam in a 0.001 *M* magnesium sulfate solution having a hydrogen-ion concentration of 10^{-10} is equal to -1.46 volts. The overvoltage of hydrogen on mercury is 1 volt; the potential of the oxygen anode is $+1.5$ volts. What is the magnesium-ion concentration when hydrogen begins to be liberated? *Ans.* 2.14×10^{-8} molar.

8. A bromide solution is electrolyzed with a silver anode. What is the reaction occurring at the anode? How much of the anode reaction product is formed by a current of 0.1 ampere in one minute? *Ans.* 0.01168 g.

9. The potential Cu | 0.1 *M* Cu^{++} is $+0.315$ volt, that of Cd | 0.1 *M* Cd^{++} is -0.43 volt. In 0.4 *M* potassium cyanide solution which is 0.1 *M* in copper, the potential of copper is -0.97 volt; in 0.4 *M* cyanide which is 0.1 *M* in cadmium, the cadmium potential is -0.87 volt. (a) Is it possible in the absence of cyanide to plate out the copper quantitatively in the presence of cadmium? (b) Which metal plates out first in 0.4 *M* cyanide? (c) Calculate the cadmium concentration in the 0.4 *M* cyanide solution when the cathode potential has become -0.96 volt. Assume that all the cadmium is present as $Cd(CN)^{=}_{4}$ and that the cyanide concentration remains unchanged during the electrolysis. *Ans.* (c) 10^{-4} *M*.

10. A solution which is 0.1 *M* in ferric and 0.1 *M* in ferrous sulfate is electrolyzed between two platinum electrodes, the solution being stirred vigorously. (a) What is the decomposition voltage? (b) What reactions occur at the cathode and at the anode? (c) How does the composition of the solution change during the electrolysis?

11. The hydrogen overvoltage on mercury is taken equal to 1 volt. The normal potential of zinc is equal to -0.76 volt. A solution of zinc perchlorate in 1 *M* perchloric acid is electrolyzed at a mercury cathode, the potential of the latter being kept at -0.97 volt. (a) What is the final zinc concentration in the solution? (b) Does hydrogen evolution interfere with the electrolysis of the zinc? *Ans.* (a) 10^{-7} *M*. (b) No.

12. The overvoltage of lead on platinum is zero; the anodic overvoltage of oxygen is 0.47 volt. The equilibrium potential (not including overvoltage) of Pt | O_2, 1 *M* $HClO_4$ is equal to $+1.23$ volts; the normal potential of lead is -0.13 volt. A solution of 1 *M* lead perchlorate in 1 *M* perchloric acid is electrolyzed between two platinum electrodes. (a) Calculate the decomposition voltage. (b) Calculate the decomposition voltage of the 1 *M* lead perchlorate solution in a buffer solution with a pH of 4.
Ans. (a) 1.83 volts; (b) 1.59 volts.

PRACTICAL PART: GENERAL

CHAPTER XI

REAGENTS

Reinheit der Substanzen ist die Feinheit des Ganzen.

Solid reagents.

In quantitative analysis only chemicals of the highest purity should be used as a rule; impure reagents may entirely vitiate the results of an analysis. The U.S.P. grade of chemical (conforming to the standards of the United States Pharmacopoeia) is usually less pure than the C.P. ("chemically pure") grade, and the latter less so than the "analyzed" or "guaranteed." The "analyzed," or reagent quality of chemical as it is also called, usually comes with a label bearing a statement of the percentages of the important impurities present. Only the reagent grade of chemical should, in general, be used in quantitative analysis.[1] Analyzed reagents should conform to the specifications of the American Chemical Society Committee on Guaranteed Reagents.[2] The statement of analysis on the bottle must not be accepted, however, as always indicating the true amounts of impurities present.

There are several reasons for not relying implicitly on the statement of analysis:

1. The analysis of the manufacturer may not always be correct, owing to the use of faulty methods or for other reasons.
2. Certain impurities may not have been tested for at all.
3. In the packing of the chemical, foreign material such as dust, bits of cork, paper, etc., may have been introduced.
4. The reagent may have been contaminated after its receipt from the manufacturer if the bottle has been opened. Stoppers may have been inter-

---

[1] These statements regarding the purity of the reagents to be used should not be misinterpreted to mean that in every case only the best chemical available should be employed. Naturally, in certain analyses certain impurities in a reagent may be entirely unobjectionable. An impurity may be harmful or harmless depending upon circumstances. Thus ammonium hydroxide containing ammonium carbonate may be used for precipitating ferric hydroxide in pure solutions in a gravimetric determination of iron, but not in the presence of the alkaline earth metals, which would be precipitated partially as the carbonates. It is generally best to have available the purest reagents, because usually these will be used for a variety of purposes, and an impurity that does not interfere in one analysis may do so in another. The use of the purest reagents is especially important in analyses involving separations.

[2] Am. Chem. Soc. Committee on Guaranteed Reagents, Ind. Eng. Chem. *17*, 756 (1925); *18*, 636, 759 (1926); *19*, 645, 1369 (1927); *20*, 979 (1928). Ind. Eng. Chem., Anal. Ed. *1*, 171 (1929); *2*, 351 (1930); *3*, 221 (1931); *4*, 154, 347 (1932); *5*, 289 (1933).

changed, a chemical poured back into a wrong bottle, a wrong label applied, etc. If there is any doubt as to the purity of the chemical used, it should be tested by standard methods for the impurities that would cause errors in the determination.[1] It must be realized that there is no such thing as an entirely pure reagent; however, the amount and kind of foreign substance present in a particular case may be so small that it will not affect the results. If the purest reagent obtainable is still too impure for the purpose, it must be purified by an appropriate method; or, in some cases, a blank can be run along with the determination (see p. 287) and the result corrected by applying the correction value yielded by the blank.

Purification of solids.

Some common methods of purifying soluble solids are described briefly below.

1. *Recrystallization from solution.* The most common method of purifying solids is by recrystallization from a suitable solvent, usually water. If the substance A containing a small amount of the soluble substance B as impurity is dissolved in the proper volume of hot water to give a saturated solution and the latter allowed to cool, the crystals of A deposited will usually contain a much smaller amount of B than the original substance, owing to the fact that the cooled saturated solution of A will generally not be saturated with respect to B, which therefore remains in solution. The recrystallized salt will not be entirely free from the impurity even if carefully washed, because crystals separating from a solution always contain included mother liquor in the form of vacuoles (p. 137), the amount of liquid thus held often amounting to a few tenths of a per cent. By a second recrystallization A can be obtained virtually free from B.

In purifying a solid by recrystallization, a roughly weighed amount is dissolved in a sufficient volume of water to give a saturated or nearly saturated solution at the boiling point. The hot solution is filtered to remove insoluble material, which is always present in greater or less amount. Filter paper placed in a funnel with a broken-off stem (to hinder crystallization in the funnel) may be used for filtration, but a Büchner funnel with a sintered-glass plate (p. 189) is more suitable; a coarse sintered-glass filter crucible may be employed if the volume of liquid is small. Then the filtered solution is cooled rapidly with stirring in order to form small crystals, which will include less mother liquor then coarse crystals. In the case of very soluble substances, it may be advisable to cool in a mixture of ice and water to obtain a good yield. Finally the solid is collected in a Büchner funnel with a sintered-glass disk (filter paper is often objectionable because fibers of cellulose are likely to be introduced), and as much as possible of the mother liquor is sucked off.[2] The solid may be pressed down in the funnel with the flat side of a glass stopper or the like, to aid in removing the liquid. To remove adherent solution, the crystals are washed with small portions of cold water, suction being applied after each addition. The recrystallized salt, if sufficiently purified by one recrystallization, is dried at or above room temperature, depending upon the material. The solid thus dried will contain included (vacuole) water unless it has been heated to a high temperature. This water may be removed by reducing the crystals to a very fine powder by grinding in an agate mortar and again heating. The complete expulsion of water is naturally necessary only when the recrystallized solid is to be used as a standard substance (p. 441). The pure dry salt thus obtained should be kept in a glass-stoppered bottle to protect it from atmospheric contamination (dust, fumes of acids and ammonia, etc.). Bottles with mouths ground on the outside (Fig. 24), instead of on the inside as usual, are very suitable for holding standard substances, especially hydrates which may lose water in air of low humidity. By lightly coating the ground-glass surface with vaseline, the bottle may be hermetically sealed, and there will be no danger of contaminating the solid with the sealing medium; furthermore, glass dust formed by rubbing the ground surfaces of stopper and bottle together cannot fall into the bottle and contaminate the solid.

---

[1] Am. Chem. Soc. Committee on Guaranteed Reagents, *loc. cit.* B. L. Murray, *Standards and Tests for Reagent Chemicals*, 2d ed., D. Van Nostrand Co., New York, 1927. G. Krauch, *Chemical Reagents, Their Uses, Methods of Testing for Purity, and Commercial Varieties*, 2d English ed., revised and enlarged by H. B. Stocks, Scott Greenwood and Son, London, 1919. E. Merck, *Prüfung der chemischen Reagenzien auf Reinheit*, 1931. *Pharmacopoeia of the United States*, Tenth Decennial revision, J. B. Lippincott Co., 1926. J. Rosin, *Reagent Chemicals and Standards*, D. Van Nostrand Co., New York, 1937.

[2] Centrifugal drainage can be used to great advantage in ridding the crystals of mother liquor. See T. W. Richards, J. Am. Chem. Soc. *27*, 104 (1905); N. F. Hall, *ibid.* *39*, 1148 (1917).

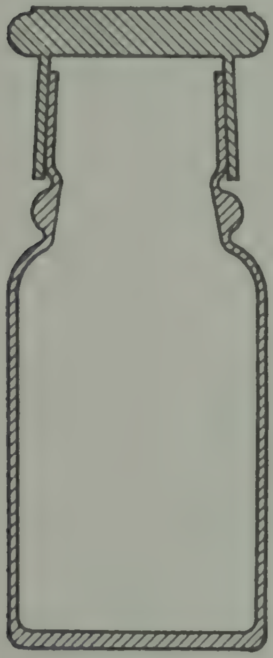


FIG. 24

Vacuole water can be removed from hydrated salts by allowing these to effloresce by placing them in an atmosphere of low humidity (in a desiccator over sulfuric acid, for example). The crystals then fall to a very fine powder, both foreign and hydrate water being lost. The substance can be rehydrated, if the hydrate is required, by exposure to an atmosphere of proper humidity (p. 131).

The following table, showing the amount of water remaining in recrystallized sodium chloride after successive heatings at various temperatures, indicates how tenaciously water may be retained in salts.

TABLE XXXII. MOISTURE CONTENT OF SODIUM CHLORIDE HEATED SUCCESSIVELY AT VARIOUS TEMPERATURES [1]

TEMPERATURE °C.	TIME OF HEATING HOURS	WATER %
180–250	4	0.19
180–250	12	0.14
295–300	12	0.09
295–300	12	0.07
380	12	0.00

If the substance to be purified is only slightly more soluble in hot water than in cold, the ordinary method of crystallization is unpractical. It is then necessary to resort to *isothermal crystallization.* In this procedure the solvent is evaporated from the saturated solution at a constant temperature. For example, by boiling a saturated solution, the solid will be deposited little by little as the solvent evaporates. However, it is usually not advisable to evaporate the solvent at a high temperature because the containing vessel is likely to be attacked if made of glass or porcelain, and the substance crystallized out may be contaminated. Isothermal crystallization is best carried out at room temperature by evaporating the solution under diminished pressure in a vacuum desiccator.

---

[1] S. P. L. Sörensen, Z. anal. Chem. *44*, 149 (1905).

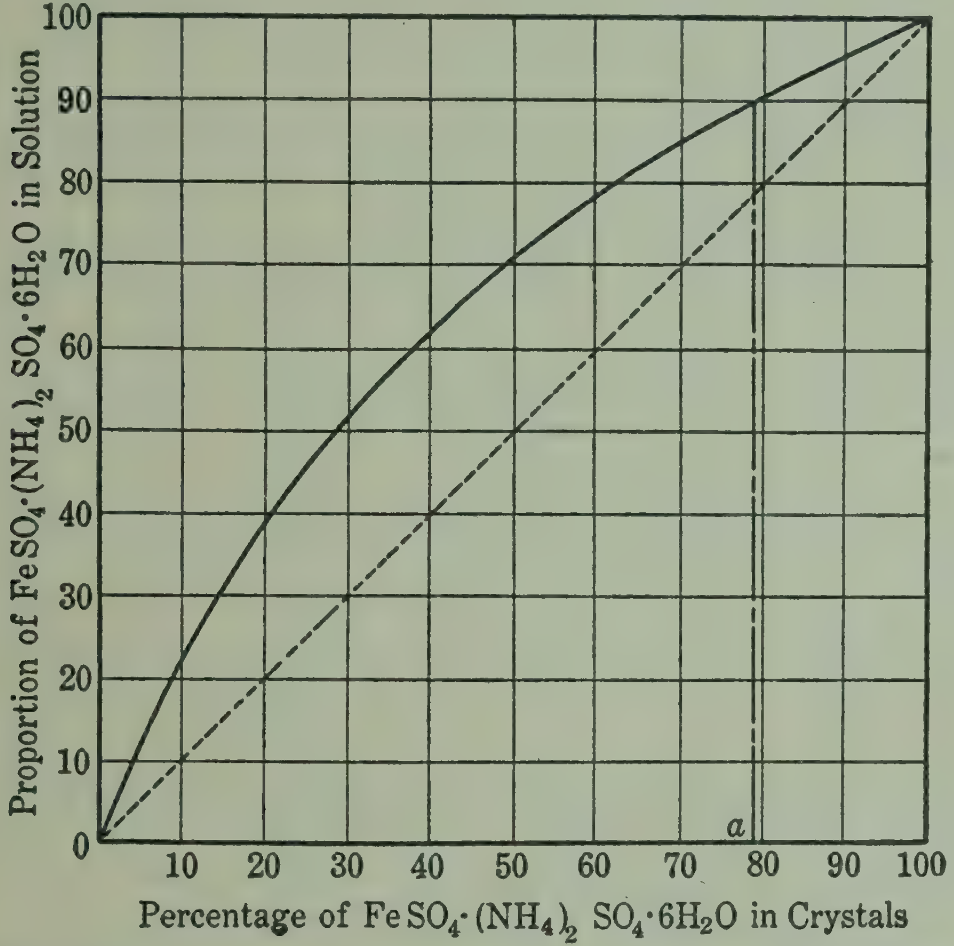


FIG. 25. The system $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6\ H_2O$–$ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6\ H_2O$. (T. V. Barker, *The Study of Crystals*, p. 124.)

Recrystallization, however, does not always lead to purification of the substance recrystallized — a fact that must always be borne in mind. Recrystallization may fail to separate B from A when A and B form mixed crystals (p. 111). In such a case more or less of B will separate with A, the exact amount depending upon the percentage of B in the original crystals, the speed of crystallization, the time of contact between crystals and mother liquor before filtration, and upon the distribution coefficient of B between A and the solution; it may even happen that B will be concentrated in the recrystallized substance. The behavior of mixed crystals of A and B on recrystallization is represented by a curve such as that given in Figure 25, which represents the composition of crystals separating from a solution of the mixed crystals ferrous ammonium sulfate hexahydrate and zinc ammonium sulfate hexahydrate. The ordinates give the composition of the solution (ranging from 100 per cent $ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6\ H_2O$ to 100 per cent $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6\ H_2O$). The composition of the first crystals separating from a solution of any composition can be read from the curve. Thus, if mixed crystals of these two sulfates containing 90 per cent of the ferrous salt are dissolved in hot water and the solution allowed to cool, the composition of the first crystals separating can be found by extending a horizontal line from the point on the Y-axis corresponding to 90 per cent of iron salt in solution to the curve (which represents the equilibrium conditions in the system: isomorphous salts in solution — isomorphous crystals) and thence down to the X-axis to the point a. The point a indicates the composition of the first crystals separating and corresponds to the composition 78 or 79 per cent $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6\,H_2O$ – 21 per cent $ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6\,H_2O$. It is seen, then, that the crystals separating are enriched in zinc salt, and this is always true no matter what the ratio of iron to zinc salt may be in the original crystals. In this case it will never be possible to free $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6\,H_2O$ from the isomorphous zinc salt by recrystallization; on the contrary, the zinc salt is concentrated in the recrystallized material. $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6\,H_2O$ (Mohr's salt) has been recommended as a primary standard in oxidimetry (p. 595); it is evident that it cannot be prepared pure by recrystallization if zinc, and other metals behaving like zinc, are present, and this is usually the case. However, it will be seen from an inspection of Figure 25 that *zinc ammonium sulfate* can be freed from the corresponding ferrous salt by a sufficient number of recrystallizations. If the zinc and iron salts were not isomorphous, a single recrystallization of zinc ammonium sulfate containing ferrous salt in small amounts would suffice to eliminate nearly all the iron. Since they are isomorphous, however, one recrystallization results in only a partial separation, the exact extent of separation depending upon how much the curve representing equilibrium conditions deviates from the diagonal line (drawn dotted in Fig. 25), which represents the case in which the crystals separating have the same composition as the solution from which they are deposited. When the equilibrium curve deviates but slightly from a straight line, it is a difficult matter to separate the two components; a great number of recrystallizations will then be necessary, and the procedure (fractional crystallization) is not suitable for analytical use.

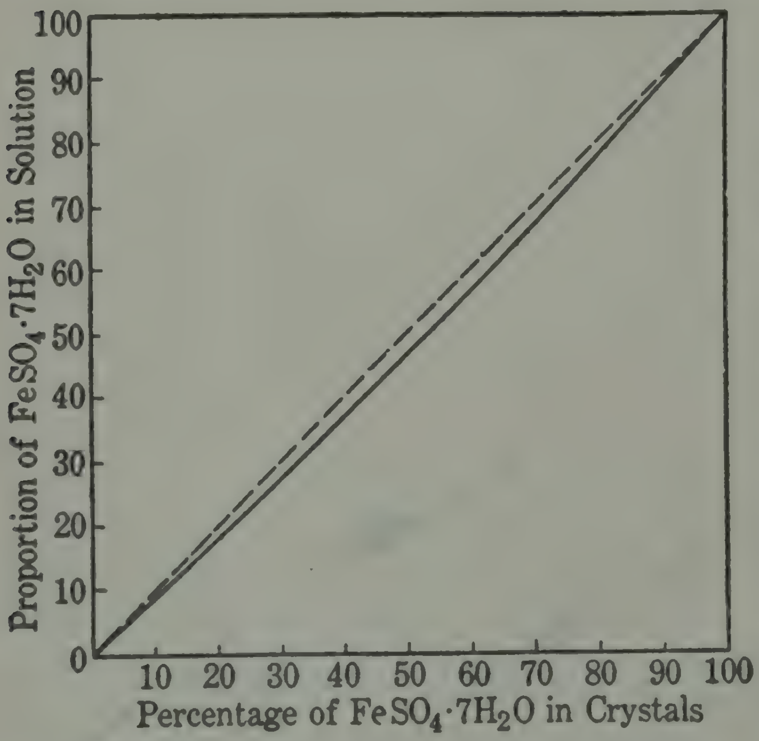


FIG. 26. The system $FeSO_4 \cdot 7\,H_2O$–$CoSO_4 \cdot 7\,H_2O$.

Figure 26 is a diagram of the system $CoSO_4 \cdot 7\,H_2O$–$FeSO_4 \cdot 7\,H_2O$. By starting with ferrous sulfate containing a small amount of cobalt sulfate, pure crystals of ferrous sulfate can be obtained by recrystallizing a sufficient number of times; but starting with cobalt sulfate containing a small amount of ferrous sulfate, the recrystallized cobalt sulfate will become richer and richer in iron. It would, therefore, be necessary to evaporate the mother liquor to obtain crystals of cobalt sulfate less rich in iron than the original and to repeat this process a great number of times — a procedure which would not be used in the purification of ordinary reagents. In such a case as this, another method of separation — one not involving recrystallization — would be used (see below, p. 168).

A third form of equilibrium curve for a binary isomorphous mixture is given in Figure 27, which represents the system ammonium magnesium sulfate–ammonium magnesium chromate.

It is clear from the above that if the impurity present in the substance to be purified forms mixed crystals with the latter, it will be difficult or even impossible to obtain the substance pure by simple recrystallization. Therefore before recrystallization is adopted as a means of purification, the literature should be consulted to determine, if possible, whether the impurities to be removed form isomorphous mixtures with the substance to be purified.

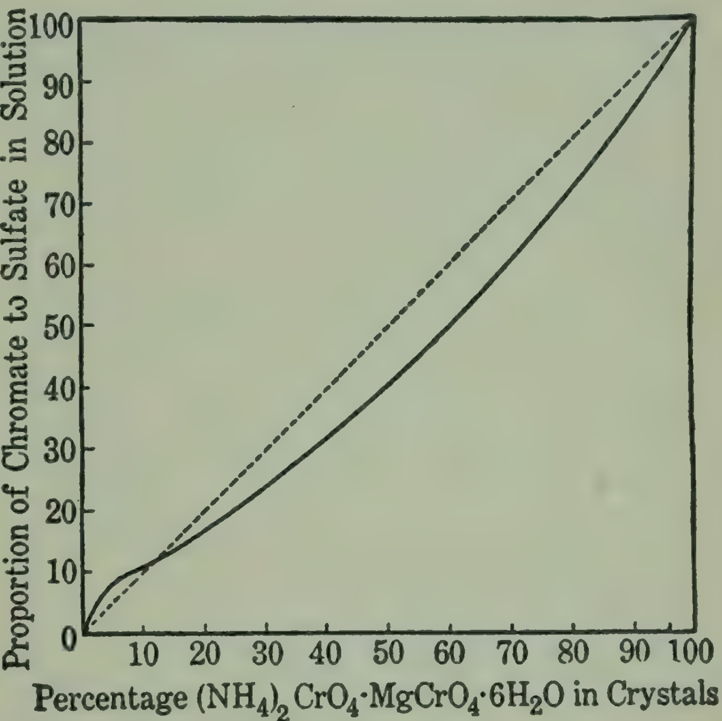


Fig. 27. The system $(NH_4)_2SO_4 \cdot MgSO_4 \cdot 6\ H_2O$–$(NH_4)_2CrO_4 \cdot MgCrO_4 \cdot 6\ H_2O$.

Even in cases where B, the impurity, is not isomorphous with A, it may happen that B will be concentrated in A on recrystallization. This phenomenon is known as anomalous mixed-crystal formation; the exact nature of the phenomenon is not understood. As an example of anomalous mixed-crystal formation, the system potassium chloride–lead chloride may be mentioned. Potassium chloride containing a small amount of lead chloride becomes continuously richer in lead as it is recrystallized.[1] Another example is afforded by ammonium chloride and ferric chloride. In spite of the fact that these two salts are not isomorphous, ammonium chloride recrystallized from a solution containing ferric chloride will always contain iron. Many other cases of anomalous mixed-crystal formation are known.

Although recrystallization is generally the best method of purifying an easily soluble solid, it is clear that it cannot always be relied upon to furnish a pure substance. Merely because a substance has been recrystallized several times, it is not permissible to conclude that it is pure. In every case the purified substance should be tested by sensitive qualitative reactions for impurities possibly present.

2. ***Precipitation by change of solvent.*** Sometimes it is not advantageous, or even possible, to purify a solid by making a saturated solution of it in hot water and then crystallizing it out by cooling the solution. The substance may decompose or undergo some other change on heating, its solubility may vary only slightly with the temperature, or it may be so soluble in water that it cannot be crystallized satisfactorily. In such cases the substance can be crys-

---

[1] R. Mumbrauer, Z. physik. Chem. A *156*, 113 (1931). H. Käding, *ibid. 162*, 174 (1932).

tallized or precipitated out of its concentrated solution by the addition of a liquid, miscible with water, in which it is much less soluble. Alcohol, in which most inorganic solids are sparingly soluble, is most commonly used. Potassium bicarbonate, which is partially decomposed into carbonate on heating above room temperature, can be purified very easily by adding alcohol to a saturated solution of the salt. The amount of alcohol, or other solvent added, must not, in any case, be so large that the impurities are also precipitated. Sodium chloride, which has a very small temperature coefficient of solubility, can be precipitated out of its saturated solution by the addition of hydrochloric acid or by passing hydrogen chloride gas into it (common-ion effect).

When this method is used, the possible effect of the included solvent must always be considered.

3. *Direct removal of impurity by physical or chemical means.* These methods sometimes render valuable service. As an example of physical removal of impurity, the removal of water by heating may be mentioned. The temperature of heating must be such that the substance dried is not decomposed or otherwise changed. Similarly, volatile acids, ammonium salts, and volatile organic compounds may often be removed by heating the material to the proper temperature.

It is sometimes possible to dissolve out or extract a foreign substance. Ferric chloride is a common impurity in aluminum chloride. It is a simple matter to extract the iron from a hydrochloric acid solution of aluminum chloride with ether. Conversely, the substance desired can sometimes be dissolved out of a mechanical mixture with an impurity. Dyes, which are usually hard to recrystallize or to precipitate, can be separated from sodium sulfate or sodium chloride, which are common contaminants, by extraction with alcohol. The dye dissolves, leaving the insoluble sodium chloride or sulfate behind.

Sometimes, if it is a matter of eliminating only one or two impurities, chemical methods can be applied. For example, potassium chloride contaminated with lead chloride can be freed from the latter by treatment with hydrogen sulfide. Lead will be precipitated as sulfide and can be filtered off. After expulsion of hydrogen sulfide, the potassium chloride solution can be evaporated down to crystallize out the salt. The potassium chloride would then have to be recrystallized to remove any sulfate, for example, formed by oxidation in the precipitation. Similarly, copper sulfate containing ferrous iron[1] can be freed from the latter by adding hydrogen peroxide to the solution to oxidize the iron and then precipitating ferric hydroxide by the addition of a little sodium hydroxide.

4. *Sublimation.* Sublimation, which is crystallization from the vapor phase, can sometimes be made the basis of purification of inorganic solids. Ammonium chloride, arsenious oxide, and iodine can be thus purified.

Not infrequently it is necessary to prepare a pure reagent by synthesis. Thus, calcium carbonate suitable for use in the J. Lawrence Smith method for the determination of the alkalies is obtained by precipitation, using pure ammonium carbonate and calcium chloride as reagents.

---

[1] Copper sulfate and ferrous sulfate cannot be readily separated by recrystallization because of the formation of isodimorphous mixtures.

Liquid reagents.

It is convenient to keep solutions of common reagents that are frequently used; yet, since most liquid reagents soon become contaminated or altered in composition, only those solutions should be prepared which are rapidly used up.

There are several reasons for avoiding the use of liquid reagents that have stood for any length of time:

1. Glass bottles in which solutions are kept are attacked to a greater or less extent depending upon the solution. Alkaline solutions especially act on glass, causing sodium, calcium, colloidal silica and silicates, etc., to go into solution and some silica to separate. Sodium hydroxide and ammonium hydroxide solutions are preferably kept in paraffin- or ceresin-coated bottles or, still better, in ceresin containers. Sodium oxalate and ammonium phosphate — $(NH_4)_2HPO_4$ — are other common reagents that act on glass. Ammonium molybdate, whether in acid or ammoniacal solution, should not be kept in glass for any length of time, because the silica introduced may cause errors in the determination of phosphorus (p. 392). Hydrofluoric acid is never kept in glass, of course, but in ceresin bottles.

2. Solutions not especially protected from the atmosphere may undergo change by absorption of carbon dioxide, oxygen, ammonia and other fumes, etc. For example, ammonium hydroxide absorbs carbon dioxide to give ammonium carbonate, an objectionable constituent of ammonia for a number of analytical uses; neutral or acid solutions of iodides liberate iodine as a result of oxidation, a reaction promoted by light; ferrous iron solutions are also oxidized; and so on.

3. Solutions may decompose spontaneously (ammonium and potassium persulfates), or by photochemical action (ammonium or sodium oxalate gives the corresponding carbonate), or as the result of bacterial action (sodium thiosulfate) and the growth of molds.

These changes may in some cases be prevented or hindered by taking precautionary measures. Bottles made of Pyrex glass are more resistant to attack by solutions than those of ordinary glass and are more suitable for holding reagents. Brown glass bottles should be used for solutions sensitive to light.

It is almost unnecessary to say that solutions, as well as solids, should be protected from external contamination. Stoppers should never be laid down upon the table top, unused portions of solution should not be returned to the bottle, and necks of bottles should be kept free from dust and deposits of ammonium salts by wiping with a *clean* damp cloth. Reagent bottles for solids as well as those for liquids are best provided with the flat-top form of stopper that projects over the lip of the bottle and to a great extent prevents the deposition of dust. Narrow-mouth (liquid) reagent bottles should best be provided with a loosely fitting cap (Fig. 28) to keep out dust and fumes. Rubber or cork stoppers should not be used for liquid-reagent bottles.

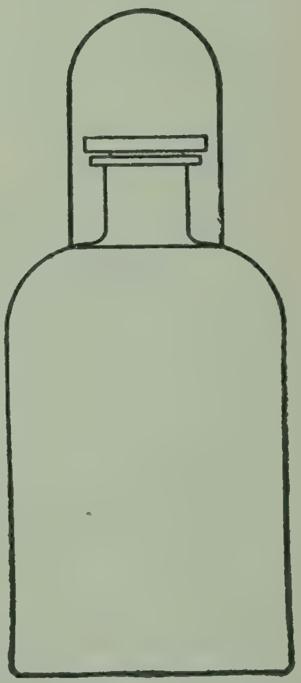


Fig. 28. Liquid reagent bottle with protecting cap.

The concentration of a liquid reagent is best expressed in terms of moles, i.e., the number (or fraction) of gram molecular weights present in one liter of solution. Thus, a solution of sodium chloride containing 29.25 g. of NaCl in one liter would be 0.50 molar $\left(\frac{29.25}{58.5} = 0.50\right)$. Molarity is designated by M; thus, in the case just mentioned, the bottle of solution would be labeled 0.50 M. Concentrations may be expressed in terms of normality, if ambiguity is not likely to arise (p. 438). It is convenient to express the strength of dilute acids and ammonium hydroxide with reference to the volume of water used to prepare them from the concentrated solutions. Thus, 1 : 5 sulfuric acid is the solution obtained by mixing one volume of concentrated sulfuric acid (sp. g. *ca.* 1.84) with five volumes of water. This diluted acid is *ca.* 6 N (see Appendix).

The common acids, hydrochloric, nitric, sulfuric, phosphoric, and acetic, can be purchased very pure and do not need to be purified for ordinary careful analytical work. If purification should ever be necessary, it is accomplished by distillation (except in the case of phosphoric acid).

Distillation is the method commonly used for purifying *liquids.* A nonvolatile impurity can be completely eliminated by distillation if precautions are taken to prevent mechanical carrying-over of the boiling liquid. Volatile impurities can sometimes be converted into nonvolatile substances and thus removed; if this is impossible, fractional distillation will separate the two substances if their boiling points are different.

Pure ammonium hydroxide is prepared most easily by passing ammonia from a cylinder into water contained in a ceresin-lined bottle which must be cooled by running water. Alternatively, the ammonia gas can be obtained by heating strong ammonia water containing a little calcium hydroxide to retain any carbonate present.

Distilled water.

Special attention must be paid to the quality of the distilled water used for analytical purposes. Since large quantities of distilled water are used in every determination, a mere trace of an impurity may cause appreciable errors. The fact that water has been distilled is no guarantee that it is pure. It sometimes happens that, owing to the use of faultily constructed apparatus, the water which has been distilled is more impure than the original. The foreign substances that may be present in distilled water include the following:

1. *Dissolved solids of the original water carried over as spray or by spurting.* Natural waters contain appreciable amounts of sodium, potassium, calcium, magnesium, iron, chloride, carbonate, and sulfate. By testing the distilled water with the appropriate reagents it is possible to tell whether these are present in significant amounts. The water may be tested directly for chloride with silver nitrate solution acidified with nitric acid, for sulfate with barium chloride acidified with acetic acid, for calcium with ammonium oxalate in ammoniacal solution, and for magnesium with titan yellow.[1] If these reactions are all negative (the solutions should be allowed to stand overnight in the precipitation tests), then the distilled water may be accepted as satisfactory for analytical use, provided it contains no suspended matter.

2. *Dissolved gases.* Of these the most objectionable is usually carbon dioxide. Distilled water often contains more carbon dioxide than the original water.

---

[1] To 10–20 ml. of water add 1 drop of 0.1 per cent titan yellow solution in water and then a few drops of 6 N sodium hydroxide. In the presence of magnesium a pink color is obtained, whereas the solution becomes orange if it is absent.

This gas may be largely removed by bubbling purified air[1] through the water for a few hours. Water thus obtained is called equilibrium water (the water being in equilibrium with the atmosphere as far as carbon dioxide is concerned) and is about 1.5×10^{-5} M with respect to carbon dioxide. Such water may be used for preparing practically carbonate-free alkali solutions (0.1 N and stronger) by dilution of strong sodium hydroxide (p. 552). Water may be entirely freed from carbon dioxide, and other gases as well, by boiling for a short time. Such water quickly absorbs carbon dioxide from the air so that if water absolutely free from carbon dioxide is required, it must be cooled and stored with protection from the air by attaching a soda-lime tube to the vessel in which it is kept. For most purposes for which "carbon dioxide-free" water is specified, equilibrium water will serve.

Distilled water always contains traces of ammonia.

3. *Dissolved material from pipes and containers.* The amount and kind of foreign material introduced in this way depend upon the equipment supplying the distilled water. Block tin and quartz are the best materials for the construction of condensers and containers, but on account of their high cost they cannot be used in the usual large installations for the production of distilled water for laboratories. Copper in very small amounts is often found in distilled water, and other metals may be present depending upon the metals with which the condensed water has come into contact.[2] The presence of copper, even in very small amounts, is often objectionable because of the catalytic properties of this metal. Thus sodium thiosulfate solutions made up with water containing minute amounts of copper decompose quite rapidly (p. 590). Distilled water which has stood for some time in glass (even in the most resistant varieties) will contain quite appreciable amounts of solids. Therefore water which is as fresh as possible should be used for analytical work.

4. *Suspended matter. Dust.* The amount of insoluble matter present in some distilled water is large enough to be a source of error in gravimetric determinations. Organic matter (probably present to a large extent as insoluble material) is objectionable because of its reactivity with various reagents (silver nitrate, potassium permanganate, etc.).

To prepare good distilled water, the distillation should first be made from alkaline permanganate solution to oxidize organic matter. The first portions of the distillate are rejected and the middle fractions collected. Water so prepared will be practically ammonia-free, since ammonia is volatilized with the first portions of the distillate. A second distillation from a slightly acid solution of sulfuric acid will remove the last traces of ammonia. Care must be taken to prevent the carrying-over of spray in the distillations. The distillate should be protected from the atmosphere to exclude acid and basic fumes of the laboratory.

---

[1] The air is bubbled through dilute sulfuric acid to remove traces of ammonia, then through water to remove droplets of acid spray, and is then drawn through a fritted-glass disk to remove dust.

[2] Traces of heavy metals (copper, lead, and zinc) in distilled water may be detected with dithizone (cf. p. 674). To detect copper, add a drop of 1 : 1 hydrochloric acid to 10 or 15 ml. of water in a 1.8 × 15 cm. glass-stoppered flat-bottomed tube and shake for one-half minute with 1 or 2 ml. of 0.001 per cent dithizone solution in pure carbon tetrachloride. If copper is present, the originally green solution of carbon tetrachloride changes to blue-green, bluish, or violet depending upon the amount of metal present. To detect lead, add a few drops of 10 per cent sodium citrate and 1 or 2 ml. of 10 per cent potassium cyanide solution to 10 ml. of the water and shake for a few seconds with 1 or 2 ml. of dithizone. If the carbon tetrachloride layer becomes pink, lead is present. Zinc may be detected by adjusting the pH of the sample to about 5 with an acetate buffer, adding 0.5 ml. of 10 per cent sodium thiosulfate to prevent the reaction of any copper or lead present, and shaking for a minute with 1 ml. of dithizone. A change in color to bluish, violet, or red shows the presence of zinc. Less than 1 microgram of each metal may be detected by these tests.

Gases.

Oxygen, hydrogen, nitrogen, chlorine, carbon dioxide, ammonia, sulfur dioxide, and hydrogen sulfide are most conveniently obtained from cylinders of the compressed or liquefied gases. Before use the gas should be purified by bubbling through appropriate solutions.[1]

Hydrogen sulfide, the most commonly used gaseous reagent, can be prepared by action of dilute acid on ferrous sulfide in a Kipp generator, if no other supply is available. The gas may be purified by bubbling it successively through saturated sodium bicarbonate solution and water. Hydrogen sulfide prepared in this way will contain considerable amounts of hydrogen derived from metallic iron in the ferrous sulfide, but this will not matter in most analytical procedures.

REFERENCES ON PURIFICATION OF SOLIDS

E. H. Archibald, *The Preparation of Pure Inorganic Substances*, John Wiley and Sons, New York, 1932.

Deals especially with purification of substances for atomic-weight determinations, but the methods described have some application in purification of analytical reagents and standard substances.

I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis*, Vol. II, Interscience Publishers, Inc., New York, 1943.

Contains directions for preparing and testing standard substances.

T. W. Richards, *Stähler's Handbuch der Arbeitsmethoden in der anorganischen Chemie*, Vol. II, 378, De Gruyter, Berlin, 1919.

General discussion of purification of substances by crystallization.

L. Vanino, *Handbuch der präparativen Chemie*, Band I, Anorganischer Teil, F. Enke, Stuttgart, 1921.

Gives directions for purifying and testing chemicals.

PROBLEM

1. (a) Assuming that the relation

$$\frac{[\mathrm{Zn(NH_4)_2(SO_4)_2 \cdot 6\ H_2O}]\ \text{cryst.}}{[\mathrm{Fe(NH_4)_2(SO_4)_2 \cdot 6\ H_2O}]\ \text{cryst.}} = K\,\frac{[\mathrm{Zn(NH_4)_2(SO_4)_2 \cdot 6\ H_2O}]\ \text{soln.}}{[\mathrm{Fe(NH_4)_2(SO_4)_2 \cdot 6\ H_2O}]\ \text{soln.}}$$

holds for the mixed-crystal system ferrous ammonium sulfate — zinc ammonium sulfate described on p. 165, calculate the value of K when the proportion of ferrous ammonium sulfate in solution is 30 : 70, 50 : 50, 70 : 30, and 90 : 10 (obtain data from Fig. 25).

---

[1] For purification of gases see L. Moser, *Die Reindarstellung von Gasen*, F. Enke, Stuttgart, 1920.

(b) Assuming that the expression given above holds during the course of the crystallization ($K = 2.5$), calculate the percentage of zinc ammonium sulfate in the crystals obtained when one half of the ferrous ammonium sulfate has been crystallized from a solution containing ferrous ammonium sulfate and zinc ammonium sulfate in the ratio 1000 : 1.

Ans. (a) $K = 2.6, 2.6, 2.4, 2.5$;
(b) 0.164 per cent.

CHAPTER XII

APPARATUS

In this chapter some facts respecting the material and construction of apparatus which have an important bearing on the proper performance of analytical work are considered.

THE MATERIALS OF ANALYTICAL UTENSILS

Glass.

In all quantitative work it is necessary to guard against the entrance of foreign substances that may directly or indirectly cause serious errors in the determinations. For this reason it is necessary to pay special attention to the quality of the glassware used to hold solutions. Beakers and flasks should be made of special resistant glass. Various kinds of chemically resistant glassware are on the market. In the United States glassware for chemical use is commonly made of Pyrex, a borosilicate glass which has many favorable properties.[1] The thermal coefficient of expansion of Pyrex glass is much lower than that of ordinary glass,[2] and therefore vessels of the former can be made much thicker to prevent breakage due to mechanical shock and still resist cracking due to rapid heating or cooling. Pyrex has a higher softening point than ordinary glass. In heating all articles of glass, care should be taken to avoid sudden temperature changes or uneven heating. Glassware should usually not be heated with a bare flame; beakers and flasks should be placed upon wire gauze.

It should be realized that Pyrex and other kinds of resistance glass, though much more resistant to the action of solutions than ordinary glass, are by no means exempt from attack. Water and solutions in general, especially when hot, act upon all varieties of glass; the amount of material brought into solution depends upon the composition of the glass, the nature of the solution, the time of contact, and so on. The data in Table XXXIII indicate to what extent Pyrex glass is attacked by some common solutions on heating. Alkaline solutions especially attack all kinds of glass. On the other hand, glass is generally acted upon only very slightly by acid solutions (except, of course, hydrofluoric acid), even to a less extent than by water.

Vycor. Recently (1940) a silica glass has been put on the market under the trade-name Vycor. It is produced by leaching a glass of special composition to leave a residue consisting essentially of silica, which is then fired at a high temperature to give a transparent vitreous product. Silica constitutes

---

[1] Another well-known resistance glass is the Jena. This is a zinc borosilicate glass.

[2] The linear coefficient of expansion of Pyrex is approximately 3.2×10^{-6}, whereas that of glass is approximately 9×10^{-6}.

Table XXXIII. Composition of Pyrex and Vycor[1]

	Pyrex[a] %	Vycor[b] %
SiO_2	81.0	96.3
B_2O_3	13.0	2.9
R_2O_3 (chiefly Al_2O_3)	2.2	0.4
ZnO	N. d.	N. d.
CaO	Negligible	Negligible
BaO	N. d.	N. d.
MgO	N. d.	N. d.
Na_2O	3.6	< 0.02
K_2O	0.2	< 0.02
As_2O_3	0.002	0.005
Sb_2O_3	N. d.	N. d.
Undetermined	—	0.3

[a] Chemical Pyrex glass (Corning No. 774).
[b] Corning Glass Works' 96 per cent silica glass No. 790.

approximately 96 per cent of this glass; the remainder of the material is chiefly boric oxide with traces of aluminum, sodium, iron, and arsenic. Because of its silica content the new glass is very resistant to the action of water and acids and may be used at temperatures up to 900°; above this temperature devitrification sets in. The linear coefficient of expansion of Vycor is 8×10^{-7} per degree Centigrade. Beakers, crucibles, evaporating dishes, flasks, etc. constructed of this new glass are obtainable.

Fused silica (fused quartz).

Fused silica is produced in two principal forms: the transparent and the translucent;[2] the former variety is better, but usually the latter can be used in place of the more expensive transparent kind. The material has a number of desirable properties. It begins to soften only at very high temperatures (above 1700° C.) and is not appreciably volatile below the softening point. However, the material begins to devitrify at 1100°–1200°, a fact to be borne in mind. Fused silica is very resistant to thermal shock owing to its very low coefficient of expansion (5×10^{-7} for the clear variety), which is about fifteen times as small as that of glass. It is not attacked by acids except hydrofluoric acid and, at high temperatures, phosphoric acid, which forms silicon phosphate. Alkaline solutions attack fused silica, especially at high temperatures (Table XXXIV); with fused alkali hydroxides and carbonates the attack is very rapid. In general silica is acted upon by the metal oxides at high temperatures, silicates being formed.[3] Fusion with alkali pyrosulfates can be made in silica crucibles if the introduction of a small amount of silica is not objectionable. Fused

---

[1] E. Wichers, A. N. Finn, and W. S. Clabaugh, Ind. Eng. Chem., Anal. Ed. *13*, 419 (1941).

[2] The translucency is due to the presence of gas bubbles. The translucent ware is obtained by fusing pure silica sand, the transparent by fusing rock crystal (quartz).

[3] Owing to its acidic character, silica is acted upon by nitrates, sulfates, and even chlorides at high temperatures.

TABLE XXXIV. CHEMICAL RESISTANCE OF PYREX AND VYCOR[1]

(Two hundred ml. of solution were boiled in a covered 250 ml. Erlenmeyer flask for 6 hours, with replenishment of the solution with water midway in the boiling.)

LIQUID	AVERAGE LOSS IN WEIGHT PER 250 ML. FLASK	
	Pyrex mg.	Vycor mg.
Water	2	1
1 *N* H_2SO_4	4	1
6 *N* HCl	22	4.5
5% NaCl	7	—
5% NaCl in 0.001 *N* HCl	Negligible	—
0.05 *N* NaOH	90	40
0.5 *N* NaOH	285	—
100 ml. NH_4OH and 100 g. NH_4Cl in 1000 ml. of aqueous solution	1.4	—
Concentrated ammonium hydroxide at room temperature for 8 and 28 days	1.9	—

silica beakers and dishes are especially valuable for evaporation of solutions that must be kept free of the alkali metals. Silica crucibles are easily electrified and slightly hygroscopic;[2] they require a much longer time for heating and cooling than do platinum crucibles, and it is more difficult to heat them to as high a temperature over a burner. Fused silica is permeable to hydrogen above 1000°. Silica glass is more brittle than ordinary glass and must therefore be protected from mechanical shock.

TABLE XXXV. ACTION OF REAGENTS ON FUSED SILICA GLASS[3]

(In each test a 76 ml. fused silica flask with 89 cm.^{2} of exposed surface was used. The tests were made with the same flask, the solutions being used in the order shown.)

REAGENT	TEMPERATURE	TIME OF EXPOSURE (DAYS)	LOSS IN WEIGHT OF FLASK (MG.)
H_2O	18°–100°	Many	0.0
NH_4OH, 10%	18°	2	0.8
NaOH, 10%	18°	2	0.4
NaOH, 30%	18°	2	0.0
KOH, 30%	18°	4	1.2
NaOH, 2 *N*	100°	3	48
Na_2CO_3, 2 *N*	100°	3	12
KOH, 2 *N*	100°	3	31
NaOH, 2 *N*	100°	3	33

---

[1] E. Wichers, A. N. Finn, and W. S. Clabaugh, Ind. Eng. Chem., Anal. Ed. *13*, 419 (1941). See also P. H. Walker and F. W. Smither, J. Ind. Eng. Chem. *9*, 1090 (1917).

[2] Hillebrand and Lundell, *Applied Inorganic Analysis*, p. 19.

[3] Mylius and Meusser, Z. Instrumentk. *44*, 221 (1905).

Porcelain.

Porcelain is generally more resistant to the action of solutions than is glass, the difference being most marked in the case of alkaline solutions. Porcelain is usually preferred to glass in evaporations and other operations in which hot liquids remain in contact with the vessel for relatively long periods of time. It should be understood, however, that quite appreciable amounts of material may be dissolved from porcelain under some conditions, and for exacting analyses it may be necessary to use platinum ware. Porcelain is mechanically stronger than glass and has a low coefficient of thermal expansion (3×10^{-6}). All porcelain vessels intended to hold liquids are glazed to prevent absorption of liquid. The resistivity of a porcelain vessel to reagents and high temperatures depends primarily upon the quality of the glaze.

Casseroles. These are lipped porcelain dishes provided with handles. They are used mostly for evaporations, especially where the liquid goes to dryness, and for heating at temperatures considerably above 100°. Since the walls of these vessels are relatively thick, they must be heated evenly and not subjected to sudden temperature changes, or else they will break.

Crucibles. Porcelain crucibles can be heated to high temperatures (1200°) and are very frequently used for igniting precipitates, because of their cheapness; they do not change in weight to any appreciable extent on strong heating. For certain common operations porcelain crucibles cannot be used at all. Fusions with sodium carbonate and other alkaline substances cannot be made in them, and hydrofluoric acid, of course, must be excluded from all porcelain ware. Pyrosulfate fusions should not be made in porcelain, although in this case the extent of attack is not very great. In certain ignitions requiring a high temperature, porcelain crucibles are less satisfactory than platinum, since the latter can be heated to a much higher temperature by the same flame. (This is not true if a furnace is used.) Thus, it is not possible to ignite calcium oxalate satisfactorily to the oxide in porcelain by heating in a gas flame, whereas the conversion is fairly easy in platinum.

Sillimanite.

By replacing the quartz and a part of the kaolin in porcelain by sillimanite ($Al_2O_3 \cdot SiO_2$), a superior porcelain is obtained.[1] The thermal coefficient of expansion of sillimanite porcelain is less than that of ordinary porcelain, and sillimanite ware is therefore less likely to break when subjected to sudden temperature changes. The material is also stronger than porcelain and is a better conductor of heat. Sillimanite crucibles are to be preferred to those of porcelain.

Platinum.

Platinum is an indispensable metal to the analyst. Without it many analytical methods would be rendered impossible.

---

[1] The somewhat unfavorable properties exhibited by porcelain on strong heating are due to the presence of free quartz grains in the material. Quartz at high temperatures is transformed into other crystalline forms with considerable changes in volume. It is this change in volume which causes strains in the porcelain which may result in cracking and weakening. Sillimanite does not show this behavior and for this reason is used to replace the quartz in the porcelain body.

Platinum has a very high melting point of 1770°. It is not altered chemically when heated in air to the highest temperatures and is not attacked to any serious extent by most reagents (exceptions are noted below). The ability of the metal to withstand the action of molten alkali carbonates and hydrofluoric acid is especially important. Platinum is a very good conductor of heat and a good radiator. It does not adsorb water vapor to any appreciable extent. For these reasons it is very suitable for the construction of crucibles for the ignition of precipitates.

Pure platinum is too soft for general use, and it is therefore always hardened and stiffened with some alloying element such as iridium or rhodium. Iridium is the metal most often used for this purpose.[1] Platinum thus alloyed, as well as the pure metal itself, is slightly volatile at elevated temperatures, a fact of which account must be taken when substances are to be weighed in platinum after strong ignition. The data in Table XXXVI will give an idea of the magnitude of the volatilization loss of platinum and its iridium and rhodium alloys. Below 900° there is no loss, at 1000° the loss is appreciable, and above this temperature it increases rapidly. Platinum alloyed with iridium loses weight more rapidly than pure platinum, owing to the greater volatility of iridium. A correction for volatility losses can be applied by running a blank with the vessel alone (p. 287). Good platinum ware should contain no other element besides the alloying element. Small amounts of iron are frequently found in platinum; it may be present at the surface of the metal as a result of the use of iron tools in the shaping of the article, but it is also present in the interior. The presence of iron is revealed by a dark color assumed by the utensil when heated to redness (formation of iron oxide). Iron is an objectionable impurity, first, because the vessel may gain in weight when heated and, second, because substances heated or treated in such platinum are likely to be contaminated. The superficial iron may be removed by treatment with hot concentrated hydrochloric acid or fused potassium pyrosulfate. Iron in the interior of the platinum will slowly diffuse out on continued heating and give ferric oxide at the surface, so that it is not easily eliminated. Other metals besides iron are sometimes found.[3]

TABLE XXXVI. APPROXIMATE LOSS IN WEIGHT, MG./100 CM.^{2}/HOUR, AT TEMPERATURES INDICATED FOR PLATINUM NEARLY FREE FROM IRON[2]

TEMPERATURE	PURE PT	PLATINUM CONTAINING:		
		1% Ir	2.5% Ir	8% Rh
900° C. or less	0	0	0	0
1000° C.	0.08	0.30	0.57	0.07
1200° C.	0.81	1.2	2.5	0.54

---

[1] Platinum-iridium alloys for chemical use ordinarily contain 0.3 to 0.5 per cent of iridium.

[2] This table is taken from G. K. Burgess and R. G. Waltenberg, Bur. Standards Sci. Paper No. 280 (1916), p. 372.

[3] Regarding the quality and testing of platinum ware and causes of decrease in weight on heating, see: G. K. Burgess and P. D. Sale, J. Ind. Eng. Chem. *6*, 452

At high temperatures platinum is permeable to various gases, especially hydrogen. This fact should be remembered when there is a possibility of reduction of the substance heated by the reducing gases of the flame.

On account of the high price of platinum in the past as compared with that of other noble metals, various alloys of the noble metals have been proposed as substitutes for platinum. Some of these substitutes have a fairly wide application, but none can entirely replace platinum. "Palau" is a gold-palladium alloy containing approximately 80 per cent of gold (m.p. 1370°). Crucibles of palau are suitable for sodium carbonate fusions[1] but not for pyrosulfate fusions. This alloy is quite strongly attacked by nitric acid. "Rhotanium" is another alloy of gold and palladium with properties similar to palau.[2] Alloys of platinum and gold have been put on the market under the names of "auranium" and "platino."

Rules for the use of platinum ware:

1. Platinum is a soft metal, even when alloyed with a small percentage of iridium, and therefore all platinum ware must be handled with care to prevent deformation and denting. Glass rods and the like should never be used to detach solids adhering to the walls of vessels, because they will scratch the metal. Neither should very hot vessels be suddenly cooled, as for example plunging a red-hot crucible into water.

2. Platinum must not be heated in contact with any other metal than itself, on account of the danger of forming alloys. Therefore only triangles of platinum, clay, sillimanite, or silica may be used for supporting crucibles of platinum; dishes should be placed on asbestos, never directly on wire gauze. Crucible tongs should preferably be platinum-tipped. However, platinum utensils may be handled with nickel tongs if allowed to cool below red heat; only solid nickel or rust-resisting iron alloy tongs should be used, never the nickel-plated or ordinary iron tongs.

3. Certain substances that directly attack platinum or will do so in the presence of another substance must be rigorously excluded from platinum. Common substances of this character are:

(a) Carbon from smoky or luminous gas flames. Platinum vessels may be heated only by nonluminous flames, and moreover they must never be allowed to come into contact with the inner cone of a gas flame which contains reducing gases. If these precautions are not observed, platinum carbide may be formed, and this compound makes platinum very brittle and liable to crack. Filter paper may be ignited in platinum without harm if the heating is gradual, so that the paper does not burst into flame, and if the carbon is burned off at a low temperature with free access of air.

(b) Compounds of the easily reducible metals and nonmetals, as well as the elements themselves. Included in this group are salts of silver, mercury,

---

(1914); *7*, 561 (1915); Bur. Standards Sci. Paper No. 254 (1915); G. K. Burgess and R. G. Waltenberg, Bur. Standards Sci. Paper No. 280 (1916); W. F. Hillebrand, P. H. Walker, and E. T. Allen, J. Ind. Eng. Chem. *3*, 686 (1911); R. W. Hall, J. Am. Chem. Soc. *22*, 494 (1900); G. A. Hulett and H. W. Berger, J. Am. Chem. Soc. *26*, 1512 (1904).

[1] H. S. Washington, J. Wash. Acad. Sci. *11*, 9 (1921).

[2] L. J. Gurevich and E. Wichers, J. Ind. Eng. Chem. *11*, 570 (1919); F. A. Fahrenwald, J. Ind. Eng. Chem. *9*, 590 (1917).

lead, bismuth, antimony, tin, etc., sulfides, and compounds of arsenic and phosphorus.[1] These may be reduced by the carbon of filter paper or by reducing gases of the flame gaining access to the interior of the crucible.

(c) Solid alkali oxides and hydroxides; barium oxide; nitrates, nitrites, and cyanides of the alkalies. All of these substances attack platinum strongly when heated or fused in it. Sodium and potassium carbonates (but not lithium carbonate) may be fused in platinum with safety.

(d) Solutions of the halogens and mixtures that furnish them, e.g., aqua regia, hydrochloric acid with oxidizing agents (permanganate, chromate, manganese dioxide, etc.). Ferric chloride in hydrochloric acid acts on platinum appreciably.

4. Substances of unknown nature should not be heated or treated in platinum.

5. All platinum ware should be kept clean and bright, inside and out. On long-continued heating, platinum becomes gray as a result of recrystallization. If the recrystallization, which begins at the surface, is allowed to continue, the vessel may eventually develop cracks; the deterioration can be stopped by burnishing the metal with moist sand composed of well-rounded grains (sea sand). In the case of a crucible this treatment may well be repeated after every five or six ignitions.

If a platinum utensil has become stained, it should be digested first in hydrochloric or nitric acid *singly*. If this treatment is without effect, potassium pyrosulfate should be fused in the vessel at a low temperature for five or ten minutes. The fused mass is poured out onto a dry stone or metal slab before it solidifies. The vessel should then be digested in hydrochloric acid, and the treatment repeated if necessary. If fusion with pyrosulfate is without effect, sodium carbonate should be tried.

It should be borne in mind that many substances heated or fused in platinum attack the metal to a slight extent. The attack may be so slight that no sensible injury is done the vessel, but the amount of platinum brought into solution in this manner may be large enough to cause an appreciable error in the determination if it is not subsequently removed. Fused alkali pyrosulfate, for example, acts on platinum slightly, so that in an ordinary pyrosulfate fusion a milligram or more of platinum may be dissolved. Sodium carbonate attacks platinum to a lesser extent than does alkali pyrosulfate; usually only a few tenths of a milligram of metal are brought into solution in a sodium carbonate fusion.

In addition to being employed for crucibles, platinum is used for dishes in which acid or alkaline liquids can be evaporated without introduction of the material of the container. Platinum is also used for electrodes (p. 421). For the use and care of platinum electrodes, see p. 422.

Gold.

Gold is an indifferent metal chemically and doubtless would find wider use in the laboratory were it not for its relatively low melting point (*ca.* 1050°). It is not attacked to any serious extent by molten alkali hydroxides and is therefore used instead of platinum for such fusions. Dishes of gold are very suitable for the evaporation of acid or basic solutions, being equal or superior to platinum for this purpose.

---

[1] Compounds of boron and silicon can be dangerous under certain conditions of high temperature and nonoxidizing environment.

Silver.

The melting point of silver is 960°, and it is therefore not safe to heat articles of this metal over a bare flame. Silver oxide is unstable at high temperatures but has a certain stability at lower temperatures (in the neighborhood of 200°), so that silver vessels may become covered with a superficial film of oxide when heated and are therefore unsuitable for weighing precipitates. Practically the only use to which silver crucibles are put in the analytical laboratory is that which involves fusion of a material with sodium or potassium hydroxide. Silver is slightly attacked by molten hydroxide at the upper edge of the melt (combined action of alkali and oxygen).[1] It is less resistant than gold to the action of molten alkalies. Silver vessels serve very well for evaporation of alkaline solutions.

Nickel.

Nickel oxidizes in air, and crucibles made of it are therefore useless for heating precipitates to be weighed. Nickel crucibles are advantageous in sodium peroxide fusions and are also suited for sodium hydroxide fusions. No metal is entirely unaffected by fused sodium peroxide. Nickel, however, is not seriously attacked, so that the same crucible can be used for a number of sodium peroxide fusions before it becomes perforated. The nickel introduced into the fusion mixture is usually unobjectionable as long as the metal does not contain the constituents being determined. Alloys of nickel and chromium (nichrome, chromel) are not easily oxidized when heated in air. A thin, firmly adherent coat of oxide is formed which protects the metal from further oxidation. Such articles as triangles, wire gauze, etc., which must withstand a high temperature in an oxidizing environment, are made of this alloy in preference to iron, which is soon destroyed and which, moreover, rusts.

Iron.

Iron crucibles, while not as durable as those of nickel, may be substituted for the latter in sodium peroxide fusions, their cheapness making up for their short life.

Crucibles for the determination of the alkalies by the J. Lawrence Smith method may be made of iron or nickel.[2]

Fused alumina.

Recently [3] highly sintered articles of pure aluminum oxide (corundum) have been produced. The refractory character (m.p. 2050°) and great hardness of corundum make these utensils of value for certain purposes.

---

[1] W. Dittmar and D. Prentice, J. Soc. Chem. Ind. *12*, 248 (1893), found that a silver crucible in which 8.5 g. of potassium hydroxide had been kept in the molten state for 10 minutes suffered a loss of 10.8 mg.

[2] A. W. Epperson and R. B. Rudy, J. Ind. Eng Chem. *17*, 35 (1925).

[3] H. Gerdien, Z. Elektrochem. *39*, 13 (1933); H. Kohl, Keram. Rundschau *41*, 30 (1933).

Alundum.

Alundum is a material composed of a high percentage of aluminum oxide with a bonding material; it is porous. Filter crucibles are made of alundum, but they are not very suitable for collecting precipitates to be weighed because it is difficult to wash soluble matter out of them, the whole crucible being porous.

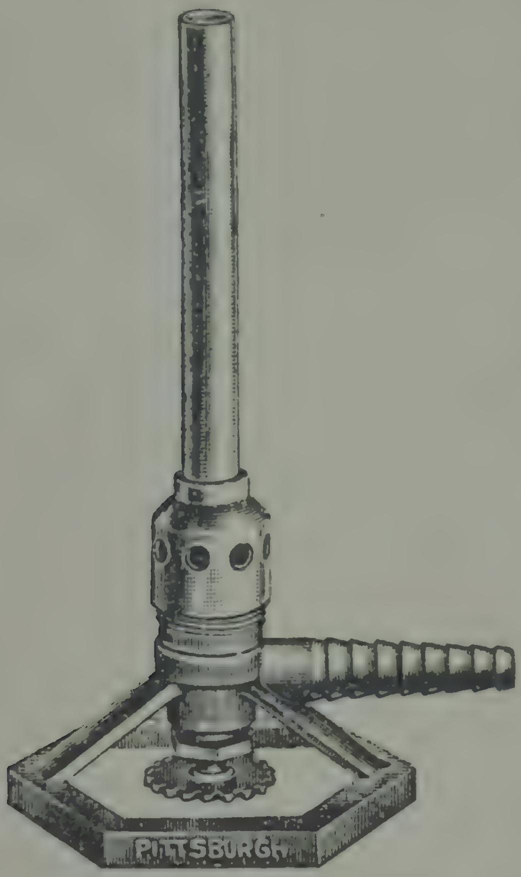


Fig. 29. Tirrill burner.

Bakelite.

This synthetic resin is well known for its resistance to hydrofluoric acid and is used for making graduates, stirring rods, funnels, etc. which are used in working with the acid at room temperature.

Heating Apparatus for Production of Medium and High Temperatures

Burners.

1. ***Tirrill.*** A Tirrill burner (Fig. 29) is an improved type of Bunsen burner in which the gas and air supply can both be regulated. With this type of burner it is possible to attain a temperature of 1000° or more in a covered platinum crucible; the maximum temperature obtainable in a porcelain crucible is considerably lower than this. Tirrill burners are generally used when a particularly hot flame is not required; many ignitions can be satisfactorily made with them.

2. ***Meker.*** The Meker burner (Fig. 30) is so constructed that the gas can be mixed with sufficient air for complete combustion without having the flame "strike back." It furnishes a very hot oxidizing flame in which a platinum crucible can be heated to a temperature of approximately 1200°. This burner is used for the ignition of precipitates that require a high temperature for complete conversion into the weighing form, and for some fusions.

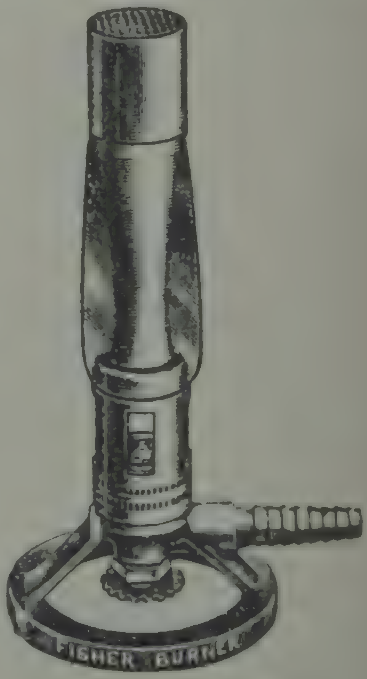


Fig. 30. Meker burner.

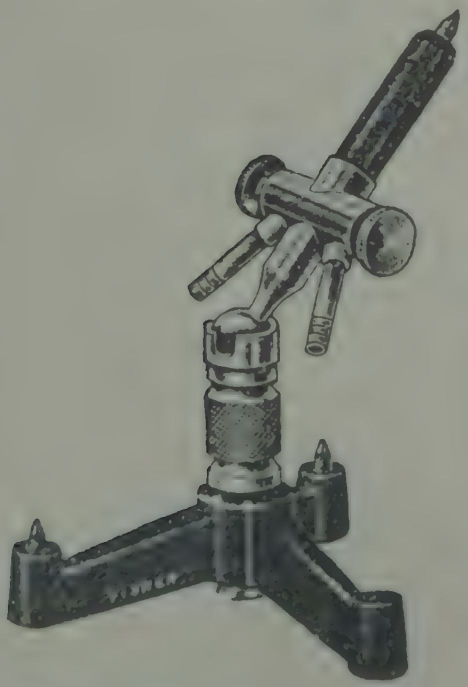


Fig. 31. Blast lamp.

3. ***Blast lamps.*** These require compressed air for operation (Fig. 31). Temperatures obtainable with a blast lamp do not much exceed those given by a Meker burner, and in most cases the latter can be used with equally satisfactory results.

Electric furnaces.

Every analytical laboratory should be provided with an electric muffle furnace capable of being heated to 1200°. It is very desirable that such a furnace be equipped with a thermocouple and an indicating pyrometer, so that the temperature can be regulated to permit the ignition of precipitates which require heating in a narrow temperature interval.

For the determination of carbon in steel, organic combustions, etc., a combustion-tube furnace is required.

Heating Apparatus for Production of Low Temperatures

Constant-temperature electric oven.

An electrically heated, thermostatically controlled drying oven having a temperature range extending from room temperature to 180°, or still better to 250°, is indispensable. It is used for drying precipitates, or solids in general, at low controlled temperatures. Liquids should not be evaporated, nor liquid mixtures digested, in drying ovens.

Hot plate.

An electrically heated hot plate capable of giving temperatures of 100°–200° should be available in the analytical laboratory. A gas-heated hot plate may be substituted.

Steam bath.

For the slow evaporation of liquids, digestion of precipitates, etc., a source of heat with a temperature not rising above 100° must be available. Such temperatures are most conveniently supplied by a steam bath. A bath connected to a steam line that can be run day and night is of great aid in expediting analytical work. In the absence of a steam bath a water bath of some kind, improvised if need be, must be used instead.

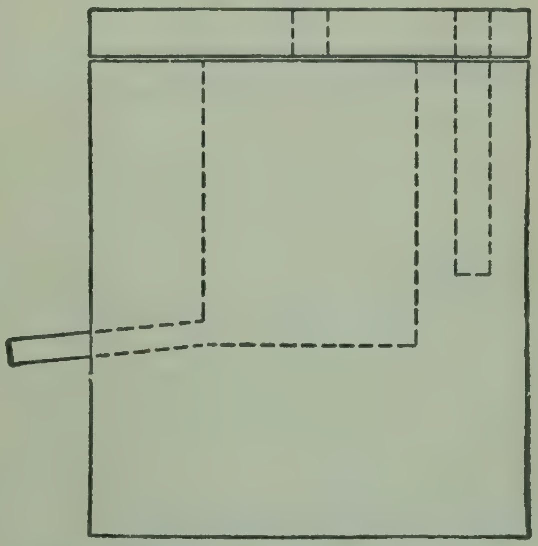


Fig. 32. Stock-Stähler block.

Stock-Stähler block.[1]

This contrivance consists of a thick hollow aluminum block heated by a burner (Fig. 32). By regulating the height of the flame, it is possible to maintain the temperature of a crucible or other vessel placed within the block constant to 5° up to temperatures of 400°. The block is a substitute for a drying oven and low-temperature furnace.

---

[1] A. Stock and A. Stähler, *Praktikum der quantitativen anorganischen Analyse*, 3d ed., p. 18, J. Springer, Berlin (1920).

Radiator.

This useful appliance (Fig. 33) is simply an air bath in which liquids can be evaporated rapidly without danger of loss. It consists of a large iron or, better, nickel crucible or special vessel fitted with a clay or silica triangle, in which the crucible containing the liquid is placed. By heating the external crucible moderately strongly with a burner, the liquid in the inner crucible can be made to evaporate rapidly without boiling. A radiator is especially valuable in the volatilization of sulfuric acid.

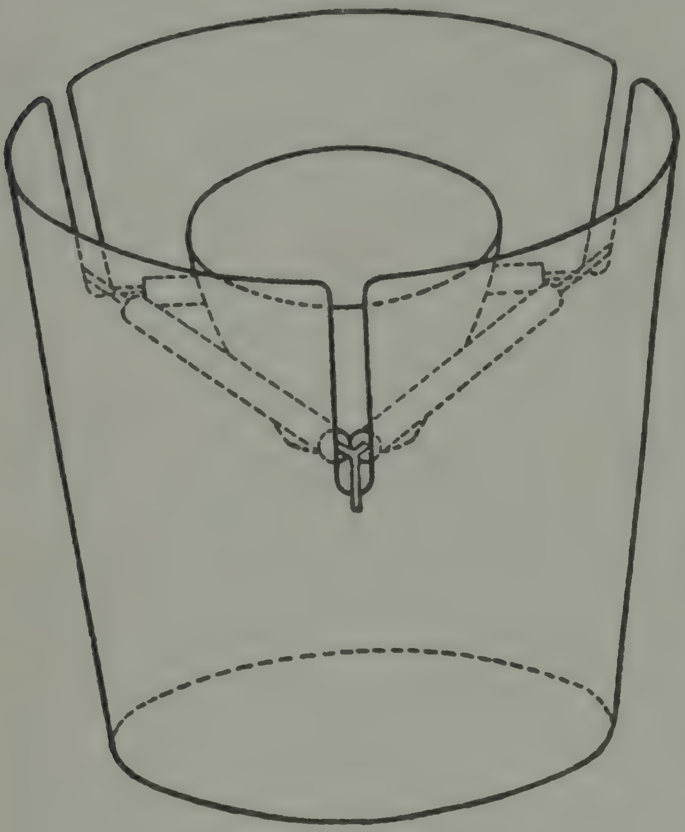


FIG. 33. Radiator.

APPARATUS FOR FILTRATION [1]

Funnels.

Funnels should be carefully selected. The angle of the cone should be 60°. The stem should not be too wide (else it will be difficult to keep it filled with liquid) and should taper slightly to the bottom (Fig. 62). Funnels are supported on a wooden filter stand.

Filter paper.

Filter paper for quantitative use must be practically ash-free. Such ash-free paper may be purchased. It has been rendered nearly free from mineral matter by digestion with hydrochloric and hydrofluoric acids followed by washing with pure water. An 11 cm. circle of quantitative ("ash-free") filter paper yields approximately 0.0001 g. of ash on ignition. Ordinary (qualitative) filter paper contains much ash and cannot be used for collecting precipitates that are later to be weighed after burning the paper.

Quantitative filter paper is made in various degrees of fineness. The choice of a particular grade of paper, as regards retentiveness, that should be used in any filtration is governed by the fineness of the precipitate to be filtered. Thus ferric hydroxide and other hydrous oxides which consist of large, slimy agglomerates are filtered through soft, loose-textured paper of relatively large pore size, which affords rapid filtration without letting any precipitate pass through. A precipitate of medium grain size, for example calcium oxalate precipitated from a weakly acid solution, may be filtered through paper of moderately fine texture, whereas barium sulfate, which usually tends to give very fine crystals, not much agglomerated, requires a dense paper which has small pores. The denser (finer) the paper the slower the filtration will be, and naturally a very fine filter paper is used only when there is an actual need for it.

---

[1] For a good discussion of all the kinds of apparatus that are used for filtration in the laboratory, see P. H. Prausnitz, Koll. Zeit. *50*, 77 (1930). Regarding apparatus for membrane filtration, see H. Biltz and W. Biltz, *Ausführung quantitativer Analysen*, p. 20 (1930).

As an example of the various grades of filter paper available, the papers of Schleicher and Schüll may be taken for illustration. The papers of each grade come in various sizes, the most commonly used circles being 5½, 7, 9, 11, and 12½ cm. in diameter. The *kind* of paper is designated by its number. Thus, Nos. 595, 597, etc., are qualitative papers, No. 575 a hardened paper, and so on. The quantitative ("ashless") papers bear the numbers 589 and 590; the most commonly used paper is the No. 589. No. 589 comes in different degrees of fineness, the retentivity being designated by the color of the band around the filters:

No. 589, black ribbon, is a soft paper of very loose texture which filters very rapidly. It is suitable for the filtration of gelatinous precipitates such as the hydrous oxides.

No. 589, white ribbon, is more retentive than the preceding and is suitable for most precipitates.

No. 589, blue ribbon, is the most retentive of all and filters rather slowly. It is intended for use with the finest precipitates.

Hardened filter paper is made by treating ash-free paper with nitric acid. It has a hard smooth surface, is quite strong when moist, and resists the action of strong acids and alkalies. It is used for filtration with vacuum, for liquids that would destroy unhardened paper, and in Büchner funnels for collecting recrystallized salts that must be kept free from filter-paper fibers.

Macerated filter paper is used as an aid to rapid filtration of gelatinous precipitates that tend to clog the pores of a filter paper. It is prepared by moistening quantitative paper with concentrated hydrochloric acid, allowing the acid to remain in contact with the paper for two or three minutes (not longer), then adding water and stirring to disintegrate the paper, and finally filtering it off and washing it with water to remove all the acid. The fibers are then suspended in water and reserved for future use. Macerated filter paper may be purchased in the form of tablets, which are disintegrated by shaking with water.

It is perhaps unnecessary to say that filter papers must be carefully protected from dust and laboratory fumes.

Filter crucibles.

For the quantitative collection of precipitates to be weighed after heating, various kinds of crucibles with porous bottoms are employed. They are all used with suction.

1. ***Gooch crucibles.*** The earliest filtering crucible suitable for analytical purposes was devised by Gooch.[1] This kind of crucible has enjoyed great popularity and is still extensively used. A Gooch crucible is a tall-form platinum or porcelain crucible (nearly always the latter) having a bottom perforated with numerous small holes. The filtering medium is a mat of asbestos fibers made by pouring a suspension of asbestos into the crucible. On applying suction, the fibers are drawn to the bottom and form a compact mat which will retain even fine-grained precipitates.

Preparation of Gooch crucible. The asbestos used should be of the long-fibered amphibole variety. To prepare the asbestos, a conveniently large amount of a good product[1] is cut to give fibers about 0.5 cm. long, macerated with water in a mortar, and digested overnight with concentrated hydrochloric acid on the steam bath. The digested suspension is filtered off on a Büchner or sintered-glass funnel, and the fibers are thoroughly washed with hot distilled water. The washed asbestos is shaken vigorously with a large volume of water, and the coarser fibers allowed to settle. The supernatant liquid containing the fine fibers is poured off into another bottle and reserved, and the coarser fibers are resuspended in a sufficient volume of water to give a thin suspension. There should be no undisintegrated asbestos remaining in the material thus prepared.[2]

---

[1] F. A. Gooch, Proc. Am. Acad. *13*, 342 (1878).

A clean Gooch crucible is placed in an adapter (Fig. 34) attached to a suction flask and is filled with a thin suspension of asbestos. Gentle suction is applied, and more asbestos poured in if necessary, so that a mat 1 to 2 mm. in thickness is finally formed. It is possible to tell when the mat has acquired the correct thickness by holding the crucible up to the light and looking through it; the outline of the holes should barely be visible. If the precipitate to be filtered is very fine, it may be advisable to put a thin layer of very fine fibers upon the mat by adding some of the special suspension (see above). A perforated porcelain plate (Witt plate) is now placed upon the asbestos mat, and a little more suspension is poured in to furnish enough asbestos barely to cover the plate and hold it in place. The Witt plate is used to protect the asbestos mat when liquid is poured into the crucible. Water must now be drawn through the crucible to wash out the loose fine fibers. The suction is increased, and water is passed through the crucible until fine fibers are no longer visible in the filtrate when examined in good light. Usually not less than a liter of water should be used for the washing. The crucible is then dried to constant weight at the same temperature to which the precipitate will be heated later.

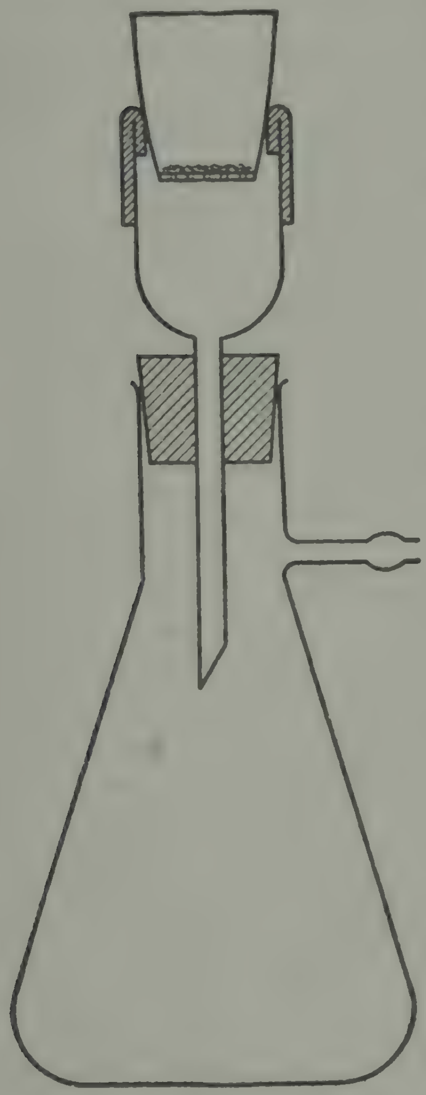


FIG. 34. Arrangement for suction filtration with Gooch and other filter crucibles.

Asbestos of the amphibole variety is very resistant to the action of dilute acids if it has been given the preliminary treatment described above. If dilute alkaline solutions are to be filtered through asbestos, the latter should be treated with hot dilute sodium hydroxide solution before being made into a mat. If there is a possibility of appreciable solvent action by the liquid filtered upon the asbestos, it is best to run a blank using the same crucible as employed in the determination. It is rather difficult to obtain an asbestos mat which is entirely stable and does not furnish a small amount of very fine fibers on continued washing. In exact work it is recommendable to filter the liquid that has passed through a Gooch crucible through quantitative paper, to ignite the latter after washing, and to weigh the residue obtained, which will then represent the asbestos lost in the filtration of the precipitate.

---

[1] The quality of asbestos on the market varies greatly; only the best available material should be used for chemical purposes.

[2] Depending upon the use to which it is to be put, the asbestos may require other additional treatment. For example, if it is to be used for filtering a permanganic acid solution, as in the bismuthate method for manganese, it should be digested with a nitric acid solution of potassium permanganate to destroy any substances that might later reduce permanganate.

Asbestos is somewhat hygroscopic; this fact should be borne in mind when using Gooch crucibles. Gooch crucibles can be heated to high temperatures. When heated over a flame, they should be placed in a porcelain capsule or ordinary crucible to prevent the entrance of gases through the asbestos.

Silica cotton has been recommended as a filtering mat in Gooch crucibles.[1] This material does not sinter below 800°, is resistant to the action of most reagents, and is nonhygroscopic.

2. ***Munroe crucibles.*** A Munroe crucible is a perforated platinum crucible having a filtering mat of porous metallic platinum.[2] This mat is prepared by covering the bottom of the crucible to a depth of 0.25 to 0.5 cm. with precipitated ammonium chloroplatinate moistened with alcohol and igniting cautiously at low redness. On heating, ammonium chloroplatinate decomposes, leaving a spongy layer of platinum which can be shaped into a coherent felt by working with a glass rod. The mat thus prepared is capable of retaining very fine precipitates.[3] Filtration is rapid. The chief advantage of this filter crucible lies in its ability to resist attack by most solutions and the possibility of heating to very high temperatures. Suitable solvents must be used to dissolve the precipitate after ignition, because the platinum mat once prepared must not be disturbed.[4]

3. ***Porous porcelain filter crucibles.***[5] In recent years porcelain crucibles having porous porcelain *bottoms* have been placed on the market.[6] These crucibles can be used in the same manner as Gooch crucibles and are more convenient because they require no preparation and do not change in weight during filtration as may happen with the latter, owing to the loss of small amounts of asbestos. They can be heated to high temperatures [7] in a furnace, or they may be placed inside an ordinary porcelain crucible or a capsule and heated with a burner. Heating and cooling should be gradual to prevent cracking.

---

[1] W. W. Russell and J. H. A. Harley, Jr., Ind. Eng. Chem., Anal. Ed. *11*, 168 (1930).

[2] C. E. Munroe, J. Anal. App. Chem. *2*, 241 (1888); Chem. News *58*, 101 (1888). This type of crucible is also known as the Neubauer crucible, Z. anal. Chem. *39*, 501 (1900). A filter crucible of porcelain with a filtering medium of porous platinum has been devised by O. Brunck, Chem. Ztg. *33*, 649 (1909).

[3] W. O. Snelling, J. Am. Chem. Soc. *31*, 456 (1909).

[4] O. D. Swett, J. Am. Chem. Soc. *31*, 928 (1909).

[5] For an extensive description and discussion of the use of porcelain, glass, and other filter crucibles see P. H. Prausnitz, *Glas- und Keramische Filter*, Akademische Verlagsgesellschaft m. b. H., Leipzig (1933).

[6] For results of tests of these crucibles, important from the analytical standpoint, see especially G. F. Hüttig and K. Schmitz, Z. anal. Chem. *64*, 224 (1924), and L. Moser and W. Maxymowicz, Chem. Ztg. *50*, 326 (1926).

[7] The weight remains constant on heating to high temperatures. Thus E. Eigenberger, Z. anal. Chem. *68*, 220 (1926) ignited a porcelain filter crucible over a blast lamp at 7-minute intervals and found the successive weights to be 21.9714, 21.9712, 21.9711, 21.9711 g.

Water, dilute acids, and ammonia do not change the weight of these crucibles appreciably (at most 0.1 to 0.2 mg.) when filtered through them, even when hot. They are, however, quite strongly attacked by alkali hydroxide solutions (Table XXXVII). They are slightly hygroscopic. A 15 g. porcelain crucible dried at 200° gained 1.0 mg. in weight after exposure to the atmosphere for one-half hour (no increase in weight after this time).[1] Attention should also be called to the fact that the temperature at which the crucible has been dried has an appreciable effect on its weight. Thus a 15 g. crucible ignited strongly was found to weigh 0.7 to 0.9 mg. less than when dried at 110° to constant weight.[2] For general use in the analytical laboratory porcelain filter crucibles are to be preferred to the glass crucibles, because the former can be heated to much higher temperatures and are therefore more generally applicable.

TABLE XXXVII. CHANGE IN WEIGHT OF POROUS PORCELAIN AND JENA GLASS FILTER CRUCIBLES TREATED WITH SODIUM HYDROXIDE SOLUTIONS[3]

(In each case the solution was allowed to remain in contact with the crucible for 2 hours. The porcelain crucible weighed *ca.* 15 g. and the glass crucible *ca.* 30 g.)

CONCENTRATION OF SODIUM HYDROXIDE SOLUTION	TEMP.	LOSS IN WEIGHT	
		Porcelain	Jena Glass
N		mg.	mg.
1/2	20°	0.5	0.1
1/8	20°	0.4	0.0
1/2	100°	46.2	9.4
1/8	100°	11.6	3.2
1/64	100°	0.7	0.0

4. ***Sintered-glass filter crucibles.*** These rather recently introduced filter crucibles (Fig. 35) are made of Pyrex or Jena glass and have a porous bottom of sintered ground glass fused on to the body of the crucible. They can be obtained in various degrees of fineness.[4]

---

[1] G. F. Hüttig and K. Schmitz, Z. anal. Chem. *64*, 224 (1924). The humidity of the atmosphere in the experiment is not stated.

[2] Moser and Maxymowicz, *loc. cit.*

[3] Partial data of L. Moser and W. Maxymowicz, Chem. Ztg. *50*, 326 (1926).

[4] Jena glass filtering apparatus is designated by certain numbers and letters. In the case of a filter crucible bearing the designation 1G4, the symbols have the following significance: the 1 indicates the size and form of the crucible, the G the kind of glass used ("Jenaer Geräteglas"), and the number 4 the grain size of the fritted-glass plate. The following are the average pore sizes of the different plates:

No.	PORE SIZE
	μ
1	100–120
2	40– 50
3	20– 30
4	5– 10

No. 3 is suitable for moderately fine precipitates, and No. 4 for very fine precipitates such as barium sulfate.

Pyrex fritted glassware is made in three porosities.

FIG. 35. Sintered-glass filter crucible.

These crucibles are used for collecting precipitates that can be dried at low temperatures. The highest temperature to which a glass crucible can be safely heated is 500°, and this only with very gradual heating and cooling. Sintered Pyrex and Jena glass crucibles are very resistant to the action of hot water and dilute acids, being the equal of, or even surpassing, the porcelain filter crucibles in this respect; but like the latter they are attacked by alkaline solutions, especially when hot, although to a smaller extent than the latter (Table XXXVII). Concentrated ammonium hydroxide is without effect.[1] Glass filter crucibles are but slightly hygroscopic (Table XXXVIII).

Quartz filter crucibles with sintered-quartz bottoms are also manufactured. They can be heated to very high temperatures.

After ignition or heating, a filter crucible containing a precipitate is cleaned by shaking out as much as possible of the solid and then dissolving the remainder in a suitable solvent.

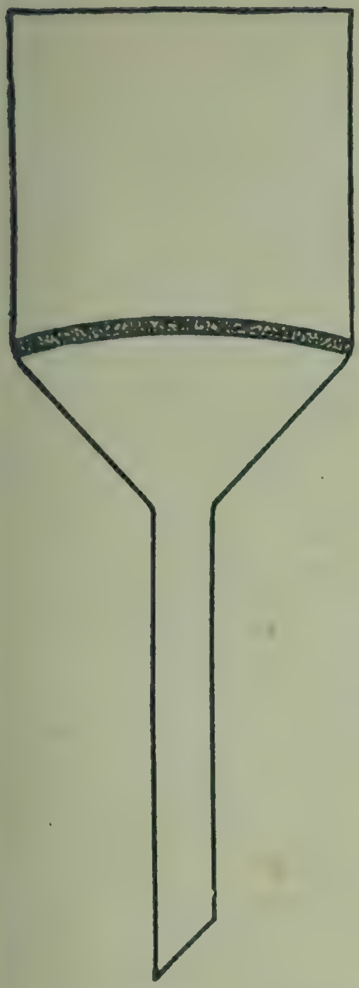


FIG. 36. Büchner funnel with sintered-glass disk.

A Büchner funnel with a sintered-glass disk (Fig. 36) is very useful for collecting salts after recrystallization.

TABLE XXXVIII. HYGROSCOPICITY OF VARIOUS TYPES OF FILTER CRUCIBLES [2]

(The crucibles were heated at 200° for 1 hr., cooled in a desiccator, then exposed to the atmosphere and weighed at various intervals as shown below. Each crucible weighed *ca.* 15 g.)

TIME AFTER REMOVAL FROM DESICCATOR	GAIN IN WEIGHT		
	Glass Crucible (G 5–6)	Brunck Crucible	Gooch Crucible
	mg.	mg.	mg.
2 min.	0.1	0.1	0.1
3 min.	0.1	0.1	0.2
5 min.	0.2	0.2	0.6
10 min.	0.3	0.5	1.2
30 min.	0.3	0.6	2.4
1 hr.	0.3	0.6	3.4
2 hrs.	0.3	0.6	4.2
6 hrs.	0.3	0.6	4.9
24 hrs.	0.3	0.6	5.2

---

[1] For data on attackability of sintered-glass crucibles by solutions, see L. Moser and W. Maxymowicz, Chem. Ztg. *48*, 693 (1924); A. Simon and W. Neth, Chem Fabrik *1*, 41 (1928).

[2] G. F. Hüttig, Z. angew. Chem. *37*, 48 (1924).

OTHER APPARATUS

Desiccators.

A desiccator is a large glass vessel, provided with a tightly fitting cover, in which the atmosphere is kept free from water vapor by a drying agent (desiccant) placed in the lower compartment of the vessel (Fig. 37). It is used chiefly for holding crucibles to protect them and their contents from moisture; these are supported above the desiccant in a porcelain plate provided with holes of suitable size for their reception. The ground-glass rim of the desiccator and that of its cover are lightly coated with vaseline or a special grease[1] to make the vessel airtight. A desiccator with a stopcock is necessary when substances are to be dried *in vacuo*. Desiccators are also used as hygrostats (p. 131) by filling the lower compartment with a solution, or mixture of solid and solution, that will give a definite water-vapor pressure.

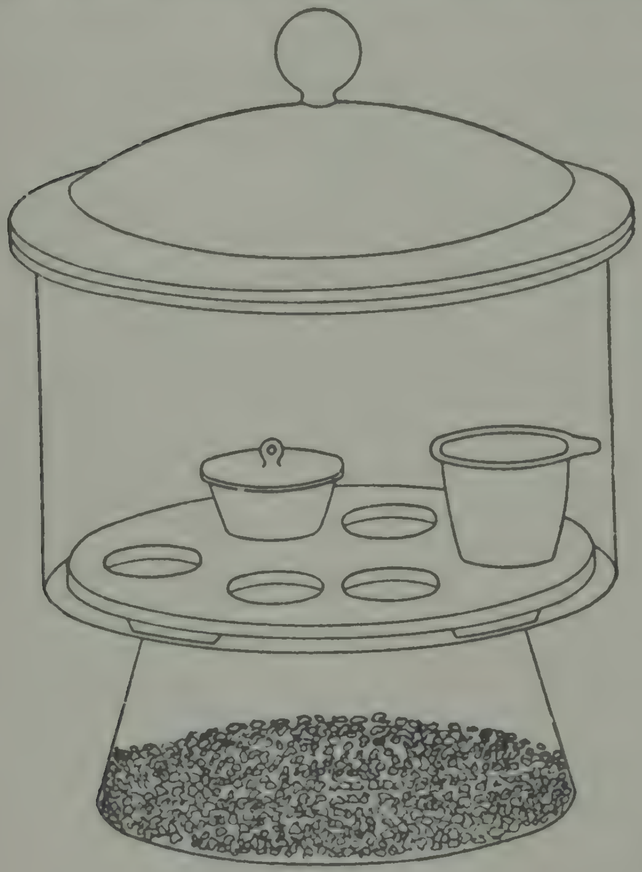


FIG. 37. Desiccator.

Desiccants. Substances which have the property of absorbing water vapor strongly through chemical or physical action are used to charge desiccators and also for drying gases and absorbing water in the determination of the latter (p. 301).

Granular or fused anhydrous calcium chloride is the drying agent most frequently used in desiccators. It is not a particularly good desiccant (see the table following), but it is satisfactory in many cases. Concentrated sulfuric acid is a more effective absorber of water than is calcium chloride; when it is used in a desiccator, the lower compartment should be partly filled with pumice, glass beads, or the like, to increase the surface of the acid exposed and to minimize splashing when the desiccator is carried about. On continued use the strong acid becomes darkened from organic matter (dust), and sulfur dioxide is liberated. Discolored acid should be replaced by fresh concentrated acid. Ignition residues such as calcium oxide and aluminum oxide which are very hygroscopic must be cooled in a desiccator charged with a powerful dehydrator, such as magnesium perchlorate, for example.

Anhydrous magnesium perchlorate[2] ("anhydrone") and magnesium perchlorate trihydrate ("dehydrite") have some favorable properties as dehydrating agents. The anhydrous salt rivals phosphorus pentoxide (probably the most powerful dehydrating agent known) in its drying power, is much more convenient to use than the latter, and can absorb approximately 50 per cent of its weight of water. The spent salt can be regenerated. Magnesium perchlorate trihydrate is suitable for use in desiccators requiring a desiccant better than calcium chloride. Anhydrous calcium sulfate[1] is one of the more powerful drying agents. Other desiccants that deserve mention are barium oxide,[2] calcium oxide, aluminum oxide,[3] and silica gel.

---

[1] A mixture of equal parts of vaseline and beeswax is very good; special mixtures are on the market. These are also used for lubricating stopcocks of burets.

[2] H. H. Willard and G. F. Smith, J. Am. Chem. Soc. *44*, 2255 (1922); G. F. Smith. *Dehydration Studies Using Anhydrous Magnesium Perchlorate*, G. F. Smith Chemical Co., Columbus, Ohio.

The following data taken from Bower[4] serve to indicate the comparative drying powers of some common desiccants.

Material	Residual Water per Liter of Air, 30.5°
	mg.
$CaCl_2$, granular (average composition $= CaCl_2 \cdot H_2O$)	1.5
$CaCl_2$, "technical anhydrous" (average composition $CaCl_2 \cdot 1/4\ H_2O$)	1.25
$Ba(ClO_4)_2$, anhydrous	0.82
NaOH, sticks	0.80
$CaCl_2$, anhydrous	0.36
$Mg(ClO_4)_2 \cdot 3\ H_2O$	0.03
Silica gel	0.03
KOH, sticks	0.014
Al_2O_3	0.005
$CaSO_4$, anhydrous	0.005
CaO	0.003
$Mg(ClO_4)_2$, anhydrous	0.002
BaO	0.0007

Wash bottles.

A wash bottle is a Florence flask fitted up to deliver a fine stream of liquid for use in the transfer and washing of precipitates. The construction of an ordinary wash bottle will be evident from Figure 38. Attention should be called to the following points: The rubber stopper should be of such size that it fits the flask tightly yet is not difficult to remove. The mouth tube is bent smoothly at an angle of 135°, and the delivery tube at an angle of 45°;[5] the latter should extend nearly to the bottom of the flask and should be bent slightly at its lower end to permit emptying the flask nearly to its last drop when inclined, as it is when used to wash precipitates. The dimensions of the mouth tube and the delivery tube should be such that the parts above the stopper lie in the same straight line; both tubes should lie in the same plane. The top of the delivery tube may extend 2 or 3 cm. above the stopper. The inclined portion of the tube should not be too long, say not more than 5 or 6 cm. The gently tapered nozzle, which should have a length of about

---

[1] W. A. Hammond and J. R. Withrow, Ind. Eng. Chem. *25*, 653, 1112 (1933).

[2] H. S. Booth and L. H. McIntyre, Ind. Eng. Chem., Anal. Ed. *2*, 12 (1930).

[3] F. M. G. Johnson, J. Am. Chem. Soc. *34*, 911 (1912); J. B. Barnitt, R. B. Derr, and E. W. Scripture, Jr., Ind. Eng. Chem., Anal. Ed. *2*, 355 (1930).

[4] J. H. Bower, Bur. Standards J. Research *12*, 241 (1934).

[5] It is almost unnecessary to say that the ends of all glass tubing must be rounded by holding in the flame after cutting.

5 cm., is connected to the delivery tube with a piece of gray rubber tubing. The orifice of the jet should be approximately 0.5 mm. in diameter so that it will deliver a rather fine stream of liquid. It is convenient to employ a 1000 ml. flask for a wash bottle intended to hold water. One or two wash bottles of 250 or 500 ml. capacity for use with liquids other than water should be at hand.

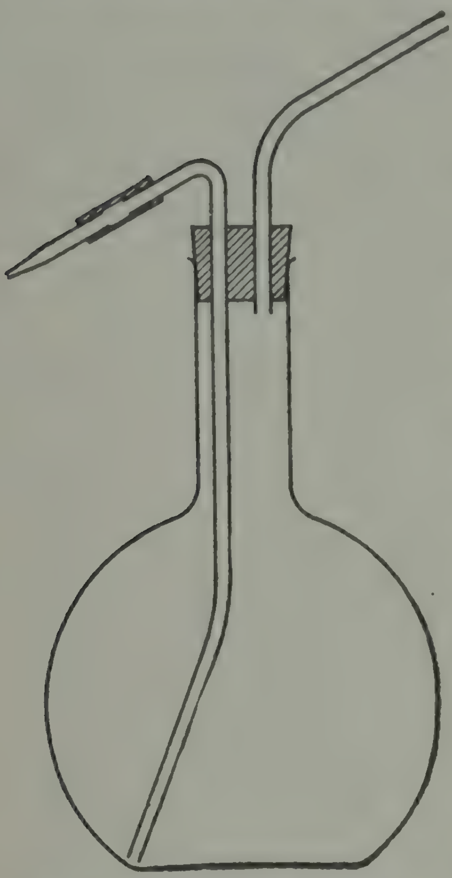


FIG. 38. Wash bottle.

Only flasks of Pyrex or similar resistant glass should be used for wash bottles. A hot-water wash bottle should have some insulating material wrapped around its neck to protect the hand. Sheet cork held in place with copper wire or cord is very suitable, as is also a wrapping of heavy cord. Asbestos paper should not be used because particles are liable to be detached from this material during use. Flasks with wicker-covered necks can be purchased. It is convenient to use a three-hole stopper in a hot-water flask, a short piece of glass tubing being inserted in the third hole. The back rush of steam into the mouth when the blowing is stopped is prevented by removing the finger from the glass tube, where it has been placed during the expulsion of the hot liquid. As soon as rubber stoppers show signs of disintegration, they should be replaced by new ones to avoid contamination by particles of rubber. All-glass wash bottles can be purchased.

Mortars.

The two kinds of mortars finding common use in the analytical laboratory are the (1) agate (Fig. 39) and (2) Plattner ("diamond") (Fig. 40) mortars. Agate mortars and pestles are used to grind substances, already coarsely powdered, to a fine powder. Samples must often be ground before they can be brought into solution or satisfactorily fused. Naturally the sample must not be contaminated in the process, and therefore agate is used for the con-

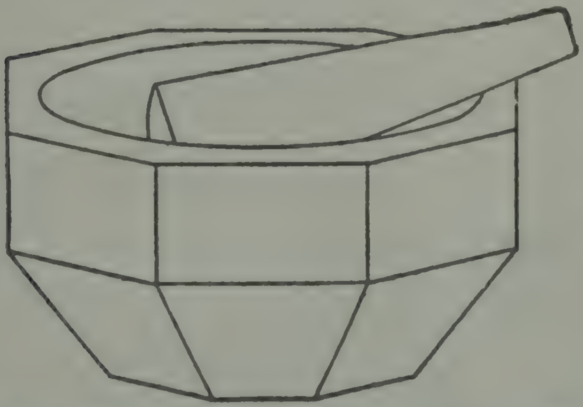


FIG. 39. Agate mortar and pestle.

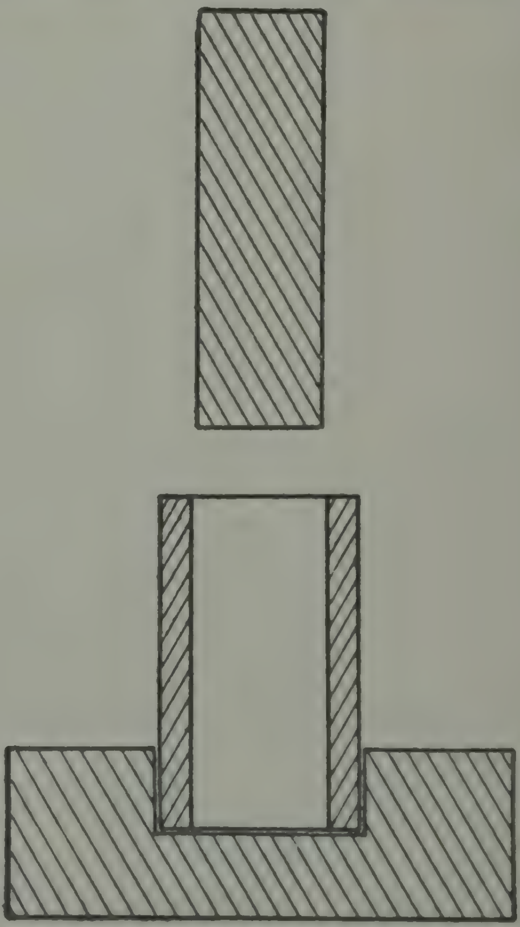


FIG. 40. Plattner mortar.

struction of such mortars because of its great hardness and therewith its great resistance to abrasion. It should be realized, however, that very hard substances ground in agate mortars may be appreciably contaminated by silica.[1] Substances should never be pounded in an agate mortar; a blow may break it. Liquids should not be allowed to stand in agate because the latter, being porous, may absorb them. Agate mortars should not be heated; such treatment may crack them.

Mullite ($3\ Al_2O_3 \cdot 2\ SiO_2$) is a substitute material for agate in analytical mortars and pestles. It has a hardness comparable to that of agate.

Porcelain mortars and pestles have no place in a quantitative laboratory. Their use is entirely inadmissible for grinding samples, which may contain hard material, and they should not be used for grinding salts on account of the danger of introducing porcelain dust.

For reducing a sample to a coarse powder that can be ground in agate, a specially constructed mortar made of hardened steel is used (see p. 735 for the use of the Plattner mortar).

It would seem that a mortar of fused alumina should be a good substitute for an agate mortar (hardness of quartz = 7, of fused alumina = 9, Mohs scale).

Balance and weights.

The balance is the most important instrument used by the analyst, and its construction and use are considered in a special chapter (Chapter XIII).

Volumetric glassware.

See Chapter XXXIII.

Colorimeter.

See Chapter XLI.

Electrolytic apparatus.

See Chapter XXVII.

Some miscellaneous items.

Stirring rods. Stirring rods are made by cutting a glass rod 3 or 4 mm. in diameter (not thicker) into suitable lengths and rounding both ends in the flame to prevent scratching the vessels in which they are used. The glass used should preferably be Pyrex. One stirring rod should be provided with a short piece of rubber tubing sealed at one end ("policeman") for removing particles of precipitate adhering to walls of vessels (Fig. 61). The rubber should fit the rod tightly.

Watch glasses. These should preferably be of Pyrex.

Wire gauze. Squares of wire gauze are used to support beakers, flasks, etc., when heated over a flame. They are commonly made of steel wire, but gauze of nichrome or chromel is to be preferred because it is nonrusting and lasts much longer. For heating platinum dishes, squares with asbestos-covered centers are used.

---

[1] This is especially true in silicate analysis, where many very hard materials are encountered. Fortunately, all samples of this nature contain high percentages of silica, so that if 0.05 per cent, let us say, of abraded silica were added to the sample in the grinding, no serious error would result.

Triangles. These are used to support crucibles when heated with a burner. Because of their cheapness, pipestem clay triangles with steel wire are often used. Triangles of nichrome or chromel wire covered with sillimanite or, better, with fused silica are very durable and are much to be preferred to the clay pipestem variety. Triangles constructed entirely of fused silica can also be obtained but possess no advantages over the silica-wire variety.

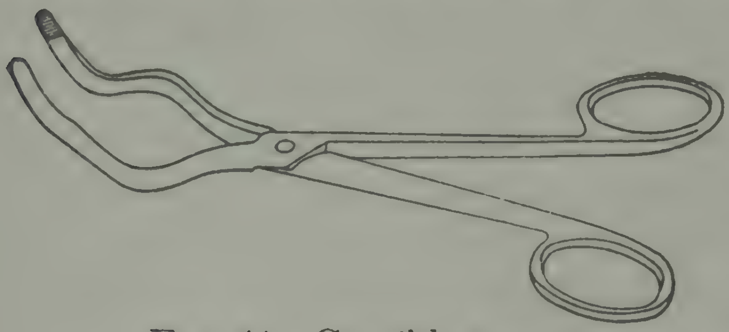


FIG. 41. Crucible tongs.

Tongs (double-bent form). As already mentioned, these (Fig. 41) should be of solid nickel or some rustless iron alloy. For handling platinum utensils it is desirable, but not strictly necessary, to have platinum-tipped tongs. If platinum vessels are allowed to cool below redness, they may be handled with pure nickel tongs or, better, with nickel tongs having chromel tips.

Desirable equipment for the analytical laboratory.

Centrifuge. An electrically driven centrifuge is a valuable adjunct to any analytical laboratory. It is used in freeing recrystallized salts from mother liquor, for collecting difficultly filterable precipitates, and for approximate quantitative analysis by measurement of the volume of centrifuged precipitates (p. 678).

Compound microscope. This instrument finds application in the analysis of heterogeneous mixtures, the examination of unknown samples, the determination of grain size of precipitates, etc.

A simple magnifier (10× or 20×) is often useful for examining samples and for other purposes.

Nephelometer. See Chapter XLII, p. 688.

Apparatus for potentiometric and conductometric measurements. See Chapter XXXII.

Refractometer (Abbe).

Apparatus for determining densities of liquids (hydrometers, Westphal balances, and pycnometers).

PROBLEM

What kind of crucible (platinum, gold, silver, nickel, iron, silica, porcelain) may be used for fusions with the following fluxes: sodium carbonate, sodium hydroxide, potassium hydroxide, sodium peroxide, potassium pyrosulfate, sodium nitrate, a mixture of sodium carbonate and sodium nitrate, and a mixture of calcium carbonate and ammonium chloride?

CHAPTER XIII

BALANCE, WEIGHTS, AND WEIGHING

> . . . *If the balance and weights are not accurate, and are not carefully taken care of, the labor and time expended on an analysis will largely go for naught. The balance and weights should therefore be regarded with a feeling akin to reverence, and the balance case looked upon, so to speak, as a sanctum sanctorum.* — H. S. Washington.

The result of a chemical analysis is usually expressed in terms of weight percentage. It is therefore necessary to determine the weight (strictly mass, as explained below) of the sample taken and the weight of the constituent sought. Every analysis involves, directly or indirectly, at least two sets of weighings. It is evident that the operation of weighing is of fundamental importance in quantitative analysis.

Principle of the method of weighing with the equal-arm balance.

Before describing in detail the construction of the analytical balance and the method of its use, it may be well to indicate the principle involved in weighing with the equal-arm balance. The analytical balance is an equal-arm balance in its ideal form.

The equal-arm balance is essentially a lever of the first class[1] in which the arms are of equal length (schematically represented in Fig. 42). Let us suppose a body having the mass M_1 is placed on the left-hand pan of the balance.[2] To obtain the "weight" of the body M_1, weights (bodies of known mass) are added to the right-hand pan until the pointer P returns to its original position.[3] Equilibrium is

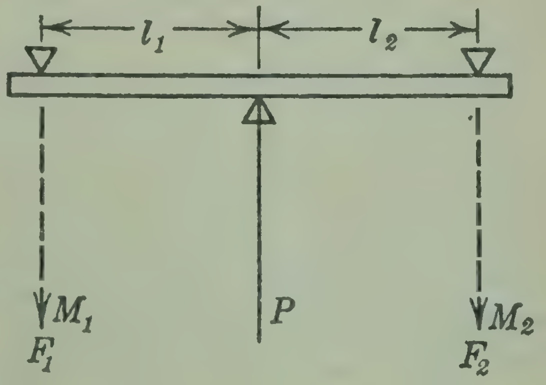


FIG. 42. Schematic representation of equal-arm balance.

---

[1] A lever in which the fulcrum lies between the points of application of the forces.

[2] By the term *mass* is meant quantity of matter. It is defined and expressed numerically by the relation $f = ma$ (Newton's second law). See any textbook of physics.

[3] To avoid introducing needless complications, due to buoyancy of the air, it is assumed that the operations are carried out *in vacuo*.

then restored, and by the principle of moments the following relation holds:

$$F_1l_1 = F_2l_2,$$

where F_1 and F_2 are the forces acting on the left- and right-hand sides of the beam (lever) at the points of suspension of the balance pans, and l_1 and l_2 are the respective distances of the points of suspension of the left and right pans from the fulcrum. Since the balance is equal-armed, $l_1 = l_2$, and at equilibrium therefore $F_1 = F_2$. The origin of the forces F_1 and F_2 lies, of course, in the attraction of the earth (gravity) on the bodies on the left- and right-hand balance pans. F_1, then, is a measure of the force exerted by gravity on the body M_1, and this strictly is the *weight* of the body M_1. The numerical value of F_1 is given by the expression

$$F_1 = M_1g,$$

where g is the acceleration of gravity.[1] In quantitative analysis we are interested in the amount of matter in a body, i.e., its mass, and not in the force with which it is attracted by the earth, i.e., its weight. In the present case we wish to determine M_1. If M_2 is the mass of the weights on the right-hand pan, it is evident that $M_1 = M_2$, because

$$\frac{F_1}{F_2} = \frac{M_1g}{M_2g} = \frac{M_1}{M_2},$$

F_1 being equal to F_2. Simple as this may appear, it is necessary to call attention to the following facts. In the first place, the equal-arm (analytical) balance is an instrument for determining mass, not weight. The value of g, the acceleration of gravity, varies from place to place on the earth's surface, depending chiefly upon the altitude and latitude of a particular locality; and therefore the weight of a body varies correspondingly. The mass of a body, however, is independent of its position on the earth. Since at any one locality the weights of bodies are proportional to their masses, g being constant, it has become customary to speak of the mass of a body as its weight; and the operation of comparing masses which is performed on the equal-arm balance has become known as weighing. It is permissible to refer to the mass of a body as its weight provided it is understood that the latter term is used as a synonym for mass and not in its strict sense.

---

[1] Again Newton's second law, i.e., a special case of $f = ma$.

The construction of the analytical balance.

An analytical balance is an equal-arm balance capable of giving the weight of a body weighing as much as 200 g. with a precision of 0.1 mg. As already indicated, it consists essentially of an equal-armed lever, supported at the center and free to swing in a vertical plane, from the ends of which are suspended two pans for the reception of the object weighed and the weights, respectively. Analytical balances differ in various constructional details, but all have the same fundamental features.

The following description applies specifically to a rider balance, a type frequently used in analytical laboratories.

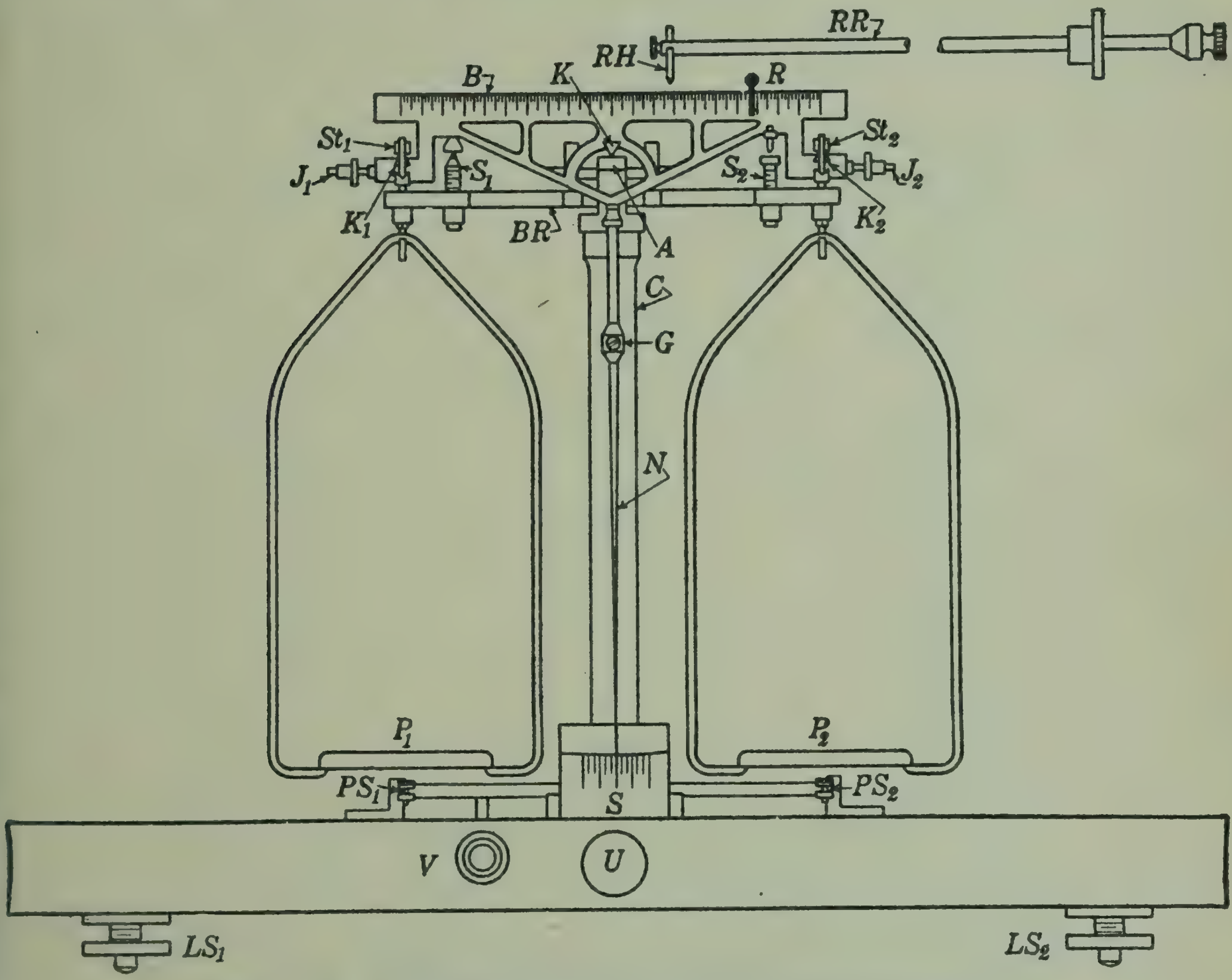


FIG. 43. Essential parts of the analytical balance.

The metal beam, *B* (Fig. 43), constructed as rigidly and as light in weight as possible, rests by means of a prism-form agate knife-edge, *K*, set in its center, upon an agate plate, *A*, placed upon the central pillar or column, *C*. The two terminal agate knife-edges, K_1 and K_2, with edges turned upwards, are mounted over the ends of the beam at equal distances from the central knife-edge. These knife-edges support the stirrups, St_1 and St_2, the contact being made against agate plates set into the tops of the latter. The pans, P_1 and P_2, are hung from the stirrups. Attached to the center of the beam and extending downward there is a long pointer, *N*, which indicates deflections of the beam from the horizontal position on the scale, *S*, at the base of the column.

To protect the knife-edges from injury when objects are placed on, or removed from, the pans, and to prevent needless wear, the moving parts of the balance can be raised so that the knife-edges and planes are very slightly separated. The device by which the beam and the stirrups are raised is called the *beam rest* or the *beam arrest*. The beam-rest crossbar, *BR*, can be raised or lowered by turning the milled head, *U*, at the base of the balance. When the beam-rest bar is raised, the studs, S_1 and S_2, engage a cam and a slot on the under side of the beam, thereby raising the latter so that the central knife-edge and its agate plane are very slightly separated. At the same time the stirrups are lifted so that the terminal knife-edges and their planes are also separated. When the balance is not in use or when objects are being placed on, or removed from, the pans, the knife-edges and planes are thus separated by raising the beam to prevent injury or dulling of the knife-edges, or grooving of the planes. The *pan-arrest* mechanism serves the purpose of keeping the pans from swinging when the beam is lowered. The pan arrests are worked by the button, *V*, at the base of the balance, to the left side of the center. When this button is pushed in, the pan supports, PS_1 and PS_2, are lowered so that the pans are free to move up and down if the beam is released. To stop the swinging of the pans or to steady them, the button is allowed to move slowly outwards; the pan rests are then elevated and barely touch the bottom of the pans, thus lightly holding them in position. The beam of the balance is graduated (sometimes only on the right-hand side) so that weight adjustments smaller than 10 mg. (sometimes 5 mg.) can be made by moving a light piece of wire along the beam. This piece of wire, the rider *R*, is bent so that it will hang on the beam. The rider is manipulated by means of the rider rod, *RR*, which can be moved above the beam, being handled by the end which extends through the balance case on the right-hand side. At its left end the rider rod is provided with a hook, *RH*, by which the rider is lifted and transferred to any part of the graduated arm. When the rider is placed on the division directly over one of the terminal knife-edges, it produces the same effect as a weight of equal mass placed on the pan below. Therefore if the division over the terminal knife-edge is numbered 10, the weight of the rider should be 10 mg.;[1] if this division is numbered 12, the weight of the rider must be 12 mg. in order that its effective weight in any position on the beam may correspond to the number of the graduation upon which it is placed. The right-hand arm of the balance is divided into 5, 10, or 12 large

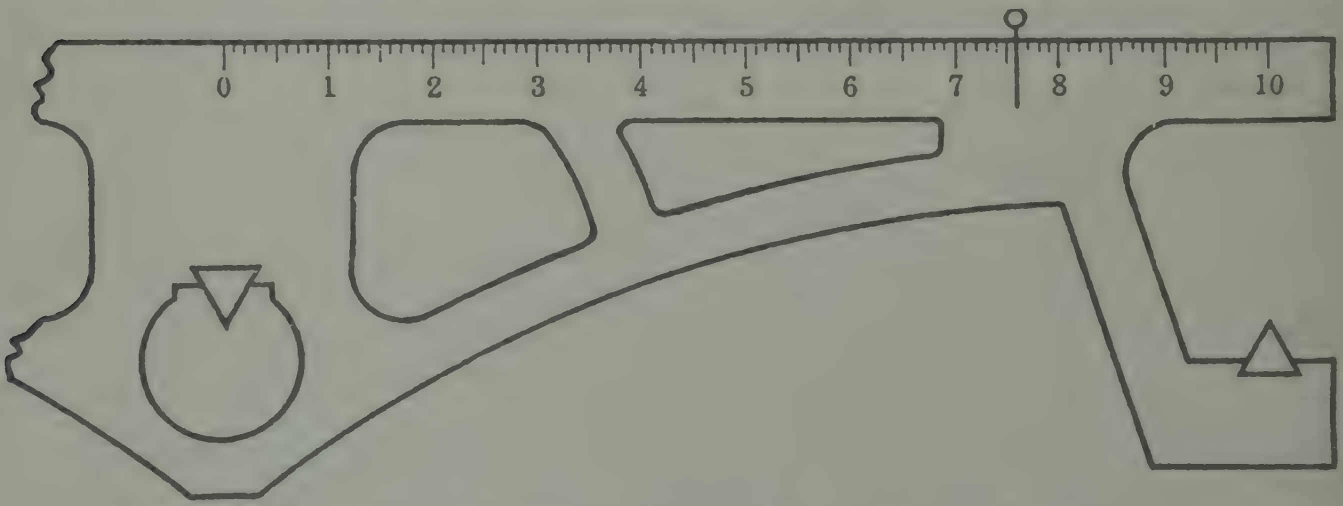


FIG. 44. Arm of a rider balance. The rider reads 7.6 mg.

---

[1] Provided that the beam is in equilibrium when the rider is over the central knife-edge. Some balances have beams graduated from 0 over the left terminal knife-edge to 10 over the right terminal knife-edge. In such a balance, the rider must be placed on 0 to maintain the beam horizontal, and the rider weighs 5 mg.

divisions, which are numbered. *The weight of the rider in milligrams should correspond to the number of divisions into which the arm is graduated from the central to the terminal knife-edge.* The large divisions are subdivided, usually into ten parts, to indicate tenths of milligrams. In this manner the weight of an object can be obtained to 0.1 mg. (Fig. 44).

A movable mass, G, is attached to the pointer for the purpose of providing a means of altering the sensitivity of the balance. By moving the weight, G, upwards, the center of gravity of the moving parts is raised, and thereby the sensitivity of the instrument is increased as will be explained later. Adjusting screws, J_1 and J_2, are placed at the ends of the beam. By moving the nuts in or out, either side of the balance can be made lighter or heavier than the other so that the beam can be made to rest horizontally when the pans are empty, if for any reason it does not do so originally.

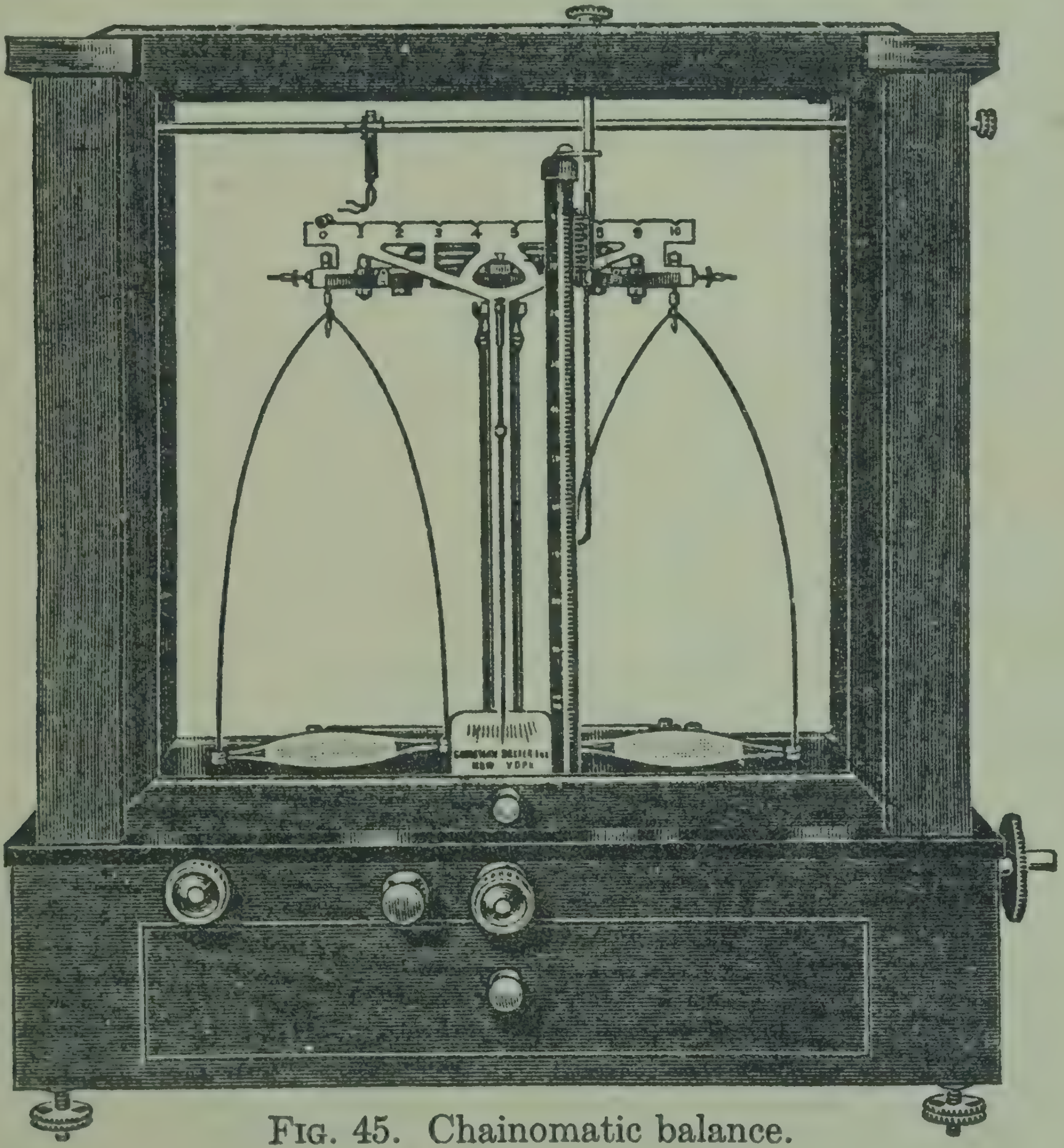


FIG. 45. Chainomatic balance.

Every balance is provided with some kind of device for indicating accurate leveling. This may consist of a plumb line suspended from the column, a pair of spirit levels, or a leveling plate. The instrument is leveled by means of the leveling screws, LS_1 and LS_2.

The balance proper is placed inside a glass case with a sliding door in front to protect it from air currents which would otherwise make accurate weighing impossible, and also to keep out dust and fumes as much as possible.

Chainomatic balances. The chainomatic balance (Fig. 45) differs from the ordinary rider balance in that weight adjustments below 50 or 100 mg. are made with a fine gold chain attached to the right-hand arm of the beam. The other end of the chain is fastened to a block which can be moved up and down a graduated pillar by turning a crank at the base of the case on the right-hand side. In this way more or less of the effective weight of the chain is transferred to the beam, the exact amount being indicated by the position of the chain on the pillar. By means of a vernier the weight on the right-hand side of the balance can be read to 0.1 mg. (Fig. 46). Some types of chainomatic balances have a beam notched at regular intervals so that by using a special rider it is possible to make weighings up to 1 g.[1] without the use of loose weights. The advantage of chainomatic balances is that weighings can be made more rapidly than with the rider type.

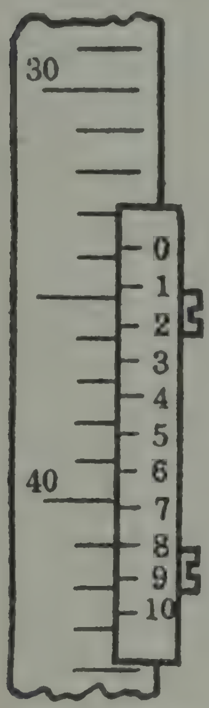


FIG. 46. The vernier reads 33.8 mg.

Air-damped and magnetic-damped balances. An air-damped balance has large pistons attached to the beam which move loosely in fixed cylinders attached to the pillar. In this way the oscillations are so completely damped that if one side of the balance is given a slight overweight, the pointer will swing to one side when the pans are released and come to rest at the end of its excursion. In weighing, the point of rest is simply noted. In some types of air-damped balances the scale is graduated to correspond to milligrams, and the point at which the pointer comes to rest is read with a microscope. In this manner weights less than 100 mg. can be read off directly to 0.1 mg. without the use of the smaller fractional weights.

Balances can also be damped magnetically by hanging a counterpoised aluminum plate from one stirrup and permitting it to swing between the poles of a permanent horseshoe magnet attached to the central pillar. The eddy currents produced in the aluminum plate when it moves in the magnetic field effectively damp the swings. It is said that ferrous materials can be weighed with this balance without error

Damping a balance in either of the above ways does not decrease its sensitivity.

Balances for special analytical work.

For obtaining the weight of small amounts of the precious metals obtained in assaying, a special type of balance, called the *assay balance*, is used. This balance is smaller and lighter than the ordinary analytical balance and has a much smaller capacity but is sensitive to 0.005 or 0.01 mg.

In microchemical analysis (p. 6) a micro balance having a sensitivity of 0.001 mg. and a capacity of 25 g. is employed. The ordinary type of micro balance is constructed in the same manner as the analytical rider balance, the only essential difference being in the size and weight of the parts.

Other balances of the analytical laboratory.

For the calibration of flasks (p. 531) and other work involving the weighing of heavy loads with a moderate degree of precision, there is required a large, sturdy equal-arm balance capable of taking a load of 2,000 g. and having a sensitivity of at least 0.01 g. at full load.

---

[1] In other types of balances a keyboard device is provided by which special weights up to 1 g. are placed on, and removed from, a bar attached to the right stirrup

A trip scale (Fig. 47) is used for weighing out rough amounts of solids or liquids in preparing reagent solutions of approximately known strength. Such a balance should have a capacity of 2 kg. and a sensitivity of approximately 0.1 g.

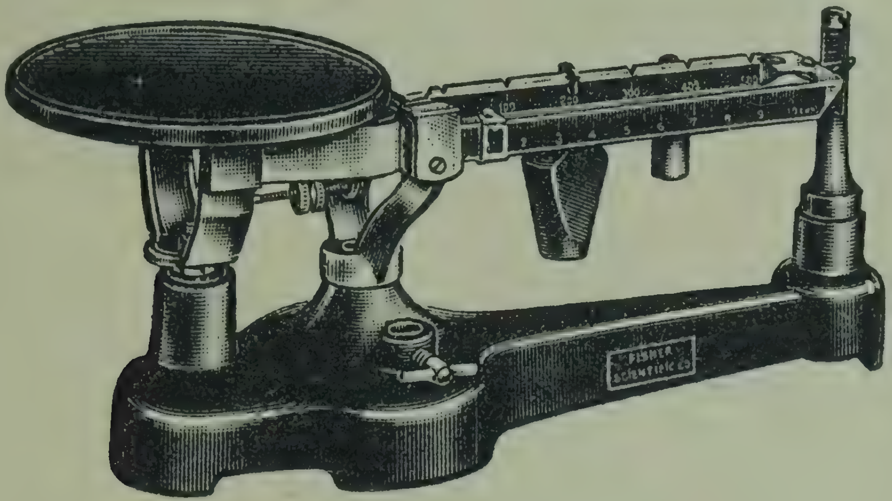


FIG. 47. Trip scale.

It is often convenient to have available a balance of 1 mg. sensitivity and a capacity of 100 or 200 g. for weighing out relatively large samples (5 g. or more) and for use with a weight buret (p. 112).

The requirements of an analytical balance.[1]

1. ***The balance must be accurate.*** This condition is fulfilled if the beam remains horizontal, i.e., retains its original equilibrium position, when equal masses are placed on the pans, and if it gives consistent weighings. In order that a balance may be accurate, the arms of the beam must be of equal length,[2] i.e., the distance of the central knife-edge from the right terminal knife-edge must be the same as that from the left, and furthermore the weights of each arm and pan must be the same (or differences compensated by movement of the adjusting screws at the ends of the beam). The consistency of a balance, denoted by the same results being obtained in successive weighings of the same object, depends largely upon the mechanical perfection of the knife-edges and the planes upon which they rest.

2. ***The balance must be stable.*** When the beam is deflected from its horizontal position, it must return to its original position of equilibrium and not remain in any position in which it is put (neutral equilibrium) or topple over (unstable equilibrium). This

---

[1] For the testing of analytical balances see A. Craig, Ind. Eng. Chem., Anal. Ed. *11*, 581 (1939); L. C. Kreider, *ibid.* *13*, 117 (1941).

[2] It being impossible to make the arms of exactly equal length, the excellence of a balance in this respect depends upon the extent to which the ideal is approached.

condition is satisfied if the center of gravity of the moving parts lies below the point of suspension (central knife-edge).

3. *The balance must be sensitive.* The sensitivity[1] of a balance is expressed by the amount of deflection of the beam or pointer produced by a small excess of weight on one of the pans. If the balance is assumed to be frictionless, the sensitivity is given by the formula:

$$\tan \alpha = \frac{wl}{Wh},$$

where

α = angle in radians through which the beam is deflected
w = excess of weight on one of the pans producing the deflection α
l = length of the balance arm (half the length of the beam)
h = distance of the center of gravity below the central knife-edge
W = mass of the moving parts (beam).

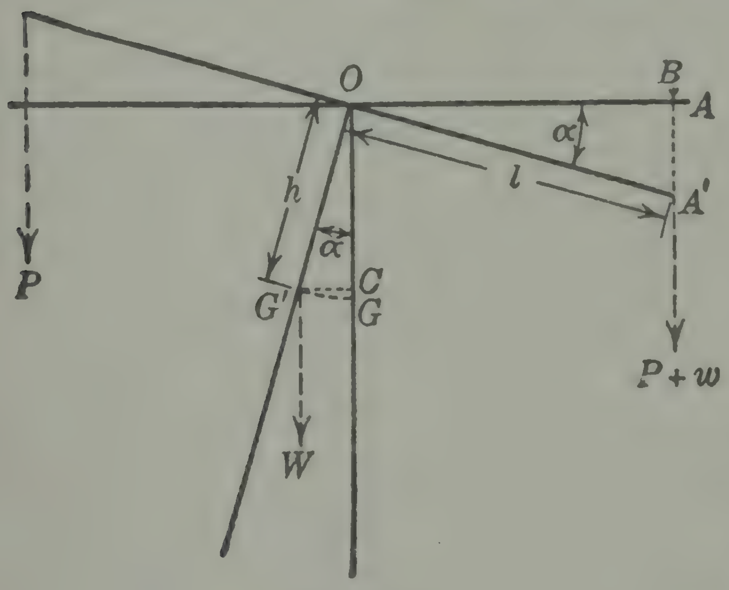


FIG. 48

Since the angle α that we are concerned with here is small, $\tan \alpha = \alpha$, and the formula becomes

$$\alpha = \frac{wl}{Wh}.$$

This formula may be derived as follows:

Let AO (Fig. 48) be the original equilibrium position of the beam, and $A'O$ the equilibrium position with the excess load w on the right-hand pan.

In the new position the forces balancing each other are $P + W$, on the left-hand side, where P = weight of the pan and W = weight of the beam, and $P + w$ on the right-hand side.

The weight of the beam acts through its center of gravity which in the new position is located at G'.

Taking moments about O, assuming both arms equal and the central and terminal knife-edges to lie in the same plane, we obtain

$$(P + w)OB = (P \times OB) + (W \times CG')$$
$$w \times OB = W \times CG'$$
$$\angle AOA' = \angle COG' = \alpha$$

But $$OB = A'O \cos \alpha = l \cos \alpha$$

and $$CG' = OG' \sin \alpha = h \sin \alpha$$

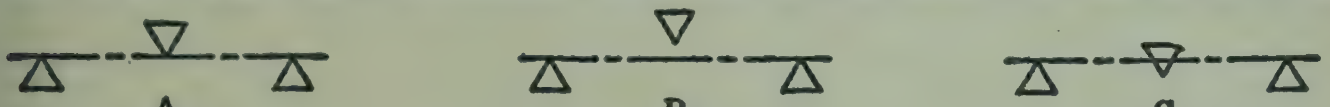
Therefore $$w \times l \cos \alpha = W \times h \sin \alpha$$

or $$\frac{\sin \alpha}{\cos \alpha} = \tan \alpha = \frac{wl}{Wh}.$$

---

[1] Called also sensitiveness and sensibility.

The sensitivity of a balance varies more or less with the load on the pans. The position of the three knife-edges with respect to each other has an important bearing on the variation of the sensitivity with the load. In general, it may be said that the central knife-edge and the terminal ones should all be in the same plane; all the knife-edges should be parallel. In Fig. 49, case *A*, the ideal arrangement of the knife-edges is represented. It is evident that changing the load on the pans in this case will not alter the position of the center of gravity if the beam is perfectly rigid, and, therefore, since *h* remains constant, the sensitivity is independent of the load. In case *B*, however, in which the plane of the terminal knife-edges is below the central knife-edge, the center of gravity is lowered by increasing the load; and since the center of gravity was below the point of suspension to begin with, the distance between the two is increased and the sensitivity is thereby decreased. This arrangement is always avoided in the construction of a balance. The converse of case *B* is the arrangement *C*, in which the plane of the terminal knife-edges is above the central edge. It is clear that here the sensitivity of the balance is increased by adding to the load on the pans, because this raises the center of gravity and decreases the distance *h*. By sufficient loading it is possible to bring the balance into neutral equilibrium and even unstable equilibrium, provided the beam is sufficiently rigid. Now actually the beam is not perfectly rigid; it bends slightly, becoming convex upwards, when a load is placed on the pans. With a good beam the bending is very slight and undetectable at small loads, but it always becomes apparent at sufficiently high loads. Therefore, if the relative arrangement of the knife-edges is that of *A* when the balance is not loaded, it will become that of *B* when object and weights are placed on the pans. Such a balance will show decreased sensitivity with increasing load, the change being a function of the load on the pans and the length and stiffness of the beam. If the sensitivity is plotted against the load, a curve such as that of Figure 50 is obtained.



A
All knife-edges in same plane

B
Plane of terminal knife-edges below central knife edge

C
Plane of terminal knife-edges above central knife-edge

FIG. 49

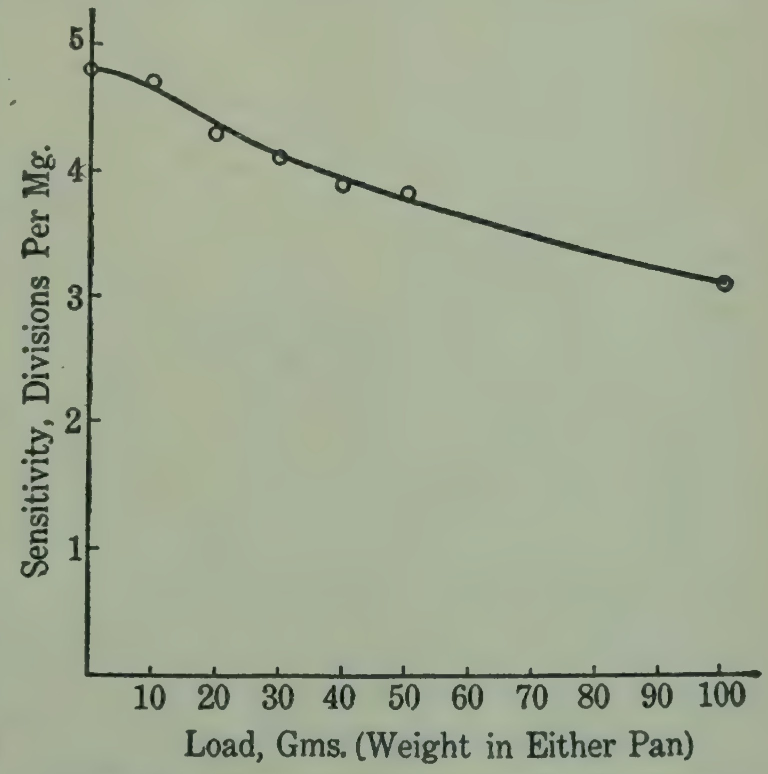


FIG. 50. Sensitivity curve of a balance.

Since it is undesirable that the sensitivity should change markedly with the load, many good balances are constructed so that the knife-edges are arranged as in C with empty pans. The distance between the central knife-edge and the plane of the terminal ones is made very small so that the balance can never become unstable. The sensitivity of such a balance may increase with the load up to a certain point and will then decrease, or the sensitivity may remain sensibly constant over a wide range of load before falling off. The reason for this behavior is very simple. Increasing the load raises the center of gravity, decreasing h; but at the same time the beam yields, decreasing the distance between the central knife-edge and the plane of the terminal knife-edges, thus increasing the value of h. If the magnitude of the two opposing effects is the same, the sensitivity remains nearly the same over a considerable range; or if the bending of the beam is not sufficiently great to counterbalance the rise of the center of gravity due to the other effect, the sensitivity will increase slightly with the load, although eventually the bending of the beam will usually gain the upper hand and then the sensitivity decreases. In any actual balance, friction in the bearings has the effect of slightly decreasing the sensitivity at higher loads.

The sensitivity of a balance should not be too great — never larger than required by the work in hand. A balance adjusted to give a deflection of 3 to 5 scale divisions per milligram has a sensitivity satisfactory for quantitative work. Quite apart from the increase in time of oscillation which accompanies increase in sensitivity, there are these objections: With high sensitivity, change in load will alter the sensitiveness greatly, and the maximum overweight that can be determined by the method of swings (*vide infra*) becomes unnecessarily small.

It is not possible to increase the sensitivity of an analytical balance to any desired value, because when the sensitivity exceeds a certain value, irregularities in the action of the balance appear. Without inquiring into the causes of erratic behavior at high sensitivities, it may be said that there is a certain limit to the accuracy with which weighings can be made with any balance, this limit being independent of the sensitivity. Therefore, for example, if the limit of precision of a balance is 0.02 mg., it is useless to adjust the sensitivity so that smaller differences than this can be detected. The reproducibility of weighings on an ordinary analytical balance should be at least 0.05 mg.

4. ***The period of swing of the balance should be short.*** This is a practical requirement. The period of oscillation of the beam of a balance is determined by the length of the beam and the distance between the center of gravity and the axis of rotation; it increases with the former and with decreasing distance between the central knife-edge and the center of gravity.[1] If the period of oscillation is too long, the process of weighing becomes tedious and requires too much time. In general, the period of swing of an ordinary analytical balance should not exceed ten seconds. The "short-arm" balances commonly

---

[1] The period of oscillation, t, is given by:

$$t = \pi \sqrt{\frac{Wk^2 + 2\,Pl^2}{Whg}}$$

where k = radius of gyration of beam and pointer
P = weight of pan and load
g = acceleration of gravity (= *ca.* 981 g./cm./sec.^{2}).

The other symbols have their previous significance.

employed in analytical practice are very quick, having a period of five to ten seconds.

Testing the precision of a balance.

Although the reproducibility of an analytical balance is nearly always good enough for ordinary analytical work, it is advisable to test a balance for its precision. This is done by repeating a weighing five or ten times and finding the average deviation (p. 273) of a single weighing, which is taken as the measure of precision. In order to reproduce the actual conditions of weighing, the object should be lifted off the pan and replaced after each weighing, and the rider should also be lifted and replaced as exactly as possible. The precision of the balance when empty and when loaded with 10 or 20 g. and with 50 g. should be obtained. It is also desirable to see what effect displacing the object or the weights from the center of the pan has on the precision. A good analytical balance may show an average deviation as small as 0.005 mg.

Weights.

The determination of the mass of an object with the equal-arm balance requires the use of a series of reference masses called *weights*.

The system of weights and measures used in scientific work is the international metric system.[1] The unit of mass in the metric system is the *gram*, which is defined as the one-thousandth part of the mass of the international prototype kilogram at the International Bureau of Weights and Measures near Paris.

Subdivisions and multiples of the gram are the following:

1 kilogram (kg.) = 1000 grams (g.)
1 decigram (dg.) = 0.1 gram
1 centigram (cg.) = 0.01 gram
1 milligram (mg.) = 0.001 gram
1 microgram (μ g. or γ) = 0.000001 gram.

Two copies of the international prototype kilogram are deposited at the National Bureau of Standards, Washington, D. C. These are known as the United States prototype kilograms. Other nations possess similar copies of the international prototype kilogram. The mass of each copy has been carefully determined by direct comparison with the international prototype kilogram. The copies of the international kilogram are used for comparison of secondary standards employed in the calibration of weights for scientific work.

An ordinary set of analytical weights includes the following pieces:[2]

Grams: (100), 50, 20, 10, 10, 5, 2, 2, 1
Milligrams: 500, 200, 100, 100, 50, 20, 10, 10, 5, 2, 2, 1
Riders.

---

[1] For a short account of the international metric system of weights and measures, see U. S. Bureau of Standards Miscellaneous Publication No. 135 (1932).

[2] Other combinations are also possible. Thus sets having the combination 1, 2, 3, 5, are now sold. Some sets have three 1 g. weights together with a 2 g. weight, instead of one 1 g. weight and two 2 g. weights. The 1, 2, 3, 5 combination saves time in calibration.

Weights smaller than 10 mg. (sometimes 5 mg.) are not actually used in weighing, since weight adjustments smaller than this are made with a rider. A chainomatic balance does not require weights smaller than 200, 100, or 50 mg., depending upon its construction; and indeed some types do not require weights smaller than 1 g., as already indicated.

The larger, or integral, weights (1 g. to 100 g.) are made of (1) brass or bronze and plated with gold, platinum, chromium, or nickel, or simply lacquered in the case of the cheaper varieties, or (2) an iron-chromium-nickel alloy. Weights of the latter material are resistant to abrasion and corrosion and are nonmagnetic. They are to be recommended.

The fractional weights (those smaller than 1 g.) are usually made of platinum, aluminum, German silver, or tantalum. The nominal mass is stamped on each weight, the numbers indicating milligrams or grams. Duplicate weights are distinguished by stamping with one and two dots (alternatively only one of the duplicates is stamped), and triplicates with one, two, and three dots. The weights are kept in a box containing compartments for each weight, the larger compartments being lined with velvet to prevent possible abrasion of the weights in removal and replacement. The weight box is provided with a cover to exclude dust when it is not being used. Weights are handled gently with bone-tipped forceps — never with the fingers. All-metal forceps should not be used.

Before a set of weights can be safely used in quantitative analysis, it must be calibrated (p. 224). No reliance can be placed upon uncalibrated weights. Weights should be recalibrated at yearly or half-yearly intervals.

TABLE XXXIX. PRECISION OF CORRECTIONS AND TOLERANCES OF CLASS S WEIGHTS TESTED AT THE UNITED STATES BUREAU OF STANDARDS

DENOMINATION	PRECISION OF CORRECTION	TOLERANCE
g.	mg.	mg.
100	0.5	0.5
50	0.1	0.3
20	0.1	0.2
10	0.05	0.15
5	0.05	0.15
2	0.05	0.10
1	0.05	0.10
mg.	mg.	mg.
500	0.01	0.05
200	0.01	0.05
100	0.01	0.05
50	0.01	0.03
20	0.01	0.03
10	0.01	0.02
5	0.01	0.02

Weights can be sent to the U. S. Bureau of Standards for testing. The Bureau of Standards recognizes two classes of analytical weights, designated respectively as Class M and Class S.[1] Class M weights include those which are used for highly accurate determinations of mass and which are to serve as reference standards for work of special precision. Class S weights comprise those that are used for ordinary accurate analytical work and similar purposes. Table XXXIX [1] gives the precision with which weights of Class S are tested at the U. S. Bureau of Standards, and the permissible tolerances.

---

[1] **Bureau Standards Circular No. 3, 3d ed. (1918).**

Weights of material not brass are usually adjusted to indicate the same weight *in air* as the same weight-piece of brass, so that all pieces of a set, no matter what their material, are consistent among themselves when the weighings are made in air.

METHODS OF WEIGHING

Direct weighing.

The object is placed on one balance pan and weights are added to the other until the beam returns to its original position of equilibrium. Then by the principle of moments the mass of the object will be equal to the mass of the weights, provided that the balance arms are of equal length, and the density of the object and the weights is the same (if the weighing is made in air). There are several methods of direct weighing, differing only in the method of determining the equilibrium position of the beam.

1. *The method of swings.* The first step in any method of weighing is the determination of the equilibrium position of the beam when the balance is empty. Since the position of the beam is indicated by the position of the pointer on the scale, it is customary to call the former the equilibrium point, the zero point, or the rest point. In the following we shall employ the term *zero point* to denote the equilibrium position of the balance when both pans are empty, and the term *rest point* to denote the equilibrium position of the balance when it is loaded.

Finding the zero point. The beam is first slowly lowered by turning the knurled head at the front base of the balance. The rider should be removed from the beam unless the beam is numbered from zero at the extreme left end, in which case the rider must be placed at the zero mark to maintain equilibrium. The knife-edges will now rest upon the agate planes, but the beam is not free to swing, because the pans are held in place by the pan arrests. The pan supports are next carefully lowered by pushing in the pan-arrest button. Now the beam is free to swing and will usually do so. If it does not or if the amplitude of the oscillations is too short, the balance door is opened and air gently wafted against the right pan with the hand, great care being taken not to touch it; or the rider may be momentarily placed upon the beam and then removed. It is convenient to have the pointer swing from three to five divisions on either side of the center mark of the scale. After the balance door has been closed, it is always best to let the beam make two or three swings before taking any readings, to let air currents subside. The farthest point reached by the pointer in each swing on both sides of the center mark of the scale is noted and recorded, the readings being made to a tenth of a division by estimation. An odd number of readings is taken on one side and an even number on the other.[1] Usually two swings are read on one side and three on the other. Readings to the right of the center mark are assigned positive values and those to the left negative values if the center division of the scale is marked zero or if the scale is not numbered.[2] Each set of readings is added separately and the average of each obtained. The algebraic sum of the averages is divided by two to obtain the mean value. The latter value is the zero point, the sign of the result indicating whether it lies to the right or the left of the center. An illustration will make the procedure clear.

---

[1] Condensed from Bureau Standards Circular No. 3, 3d ed. (1918).

Readings on Left		Readings on Right	
(1)	− 4.2	(1)	+ 4.4
(2)	− 4.0	(2)	+ 4.2
(3)	− 3.8		+ 8.6
	− 12.0		

$$\text{Average} = \frac{-12.0}{3} = -4.0 \qquad \text{Average} = \frac{+8.6}{2} = +4.3$$

$$\text{Mean} = \frac{4.3 - 4.0}{2} = \frac{+0.3}{2} = +0.15 \text{ or } +0.2 - \text{the zero point.}$$

In this case, therefore, the zero point of the balance lies 0.2 of a division to the right of the center line (the nominal zero).

In observing the swings, the eye of the observer must remain in the same position to avoid errors of parallax. The pointer should swing very close to the scale to prevent these errors as much as possible. In a well-adjusted balance the zero point will lie within one division of the zero of the scale. It is not necessary or even advisable that the two coincide. The zero point of a balance will change slightly from day to day, or even from hour to hour, owing to slight changes in temperature and other causes. If the zero point lies more than one small division from the center line of the scale, one of the adjusting nuts attached to the ends of the beam should be moved in or out to make that side of the balance heavier or lighter as the case requires.[1] The balance should then be left to itself for half an hour to allow equalization of temperature.

---

[1] One more reading must be made on one side than on the other because the oscillations necessarily become successively smaller owing to retardation by the air and by friction in the bearings. If the same number of readings were taken on both sides, the average value then obtained would not correspond to the zero point of the balance on account of the damping of the swings. However, if an even number of readings is made on one side and an odd number on the other, the average of these will give the zero point.

[2] Some prefer to number the center division of the scale 10 and thus avoid the use of positive and negative values.

Determination of sensitivity of balance at various loads. It is important to remember that the sensitivity of a balance depends upon the weight on the pans (p. 203), usually decreasing with increasing load, and it must therefore be determined for various loads. The procedure is the following. After the zero point of the balance has been obtained, the pans are arrested, and the rider is placed exactly on the 1 mg. division of the beam. The beam is then set swinging and the rest point of the balance obtained in exactly the same manner as described above. The difference in scale divisions between the zero point and the rest point expresses the sensitivity of the empty balance.[2] Thus, if the zero point of the balance is 0.2 and the rest point after adding a milligram is found to be -3.8, then the sensitivity is 1 mg. $\equiv 4.0$ divisions. In like manner the sensitivity is determined with the following weights placed successively on both pans: 5, 10, 20, 30, 40, 50, and 100 g. The rest point of the balance must be found for each set of weights before the excess milligram is added. The results should be graphed as shown in Figure 50. From this curve the sensitivity at any load can be found. The number of the balance to which these data apply should be noted on the graph.

The weighing. After the zero point, i.e., the rest point of the empty balance, and the sensitivity at various loads have been found, the object is ready to be weighed. It is customary to place the object on the left-hand pan and the weights on the right, for it is more convenient for a right-handed person to add weights to the right-hand pan. The beam must be raised and the pans arrested before an object or a weight is placed on the pans.

---

[1] The student should have the instructor make this adjustment.

[2] The sensitivity of a balance is usually expressed for practical purposes in terms of the change in the equilibrium point produced by a weight of one milligram, the change being measured in scale divisions. Sensitivity can also be stated in terms of the weight required to shift the equilibrium point one scale division. These values for sensitivity are, of course, purely arbitrary, since the length of a division or the length of the pointer is not specified, but are more convenient than the absolute values measured in radians (α).

An object is counterbalanced by adding weights in decreasing order of size. The weight estimated to be slightly heavier than the object is removed from the box *with the forceps* and placed on the right-hand pan, at the center. The beam is slowly lowered,[1] and the movement of the pointer is observed. If the mass of the object is considerably different from that of the weight, the pointer will move one way or the other in spite of the fact that the pan supports are in place, for these are depressed by an excess weight of about a gram on one of the pans. If the pointer moves to the left, the object is evidently lighter than the weight; and the latter is replaced, after the beam has been raised, by the next smaller, and the beam lowered as before. If the weight is now too small, the next smaller weight is also added and the test for equilibrium made again. Weights are thus added and removed systematically until the pointer does not move when the beam is lowered. The excess of weight on one side or the other is now too small to depress the pan supports, and further tests must be made by lowering the pan arrests so that the beam can move freely. Therefore the pan-arrest button is pushed in slightly, and the movement of the pointer is observed without letting it swing far from the center of the scale. The addition and removal of the smaller weights are continued as before, always systematically, until the object is balanced to within 5 mg. or 10 mg., depending upon the weight of the rider. It is not necessary to raise the beam when adding *fractional* weights, but the pan supports should be up. When *any* weight is *removed*, the beam must be raised and the pans arrested to prevent injury to the knife-edges. The final counterbalancing is done with the rider. The latter should be placed systematically, first near the center of the arm, then one fourth of the distance from one end, etc. In precise weighings the rider is adjusted to the nearest milligram, and the tenths (or hundredths) of a milligram are then calculated from the difference between the zero point and the rest point, the sensitivity of the balance being known for the load on the pans.[2] An example will make the method of calculation clear:

---

[1] The beam should not be lowered further than is necessary to indicate which side is heavier, i.e., the pointer should not be allowed to move more than a division or two from the center of the scale.

[2] The method of calculation is based on the assumption that the shift in the equilibrium point of the balance as indicated by a pointer playing over a scale which is a circular arc graduated in equidistant divisions is proportional to the increase in weight. For the small angles and small weights we are concerned with here, the assumption is certainly a valid one.

Zero point of balance = + 0.5

Rest point of balance when weights on pan = 14.530 g. and rider is placed on beam at 3.0 mg. = + 2.0. (Weights and rider on right side of beam.)

Sensitivity of balance at 14.5 g. load = 4.0 divisions per mg.

Evidently the object is not quite counterbalanced. It is necessary to find the position of the rider at which the rest point would coincide with the zero point. Moving the rider from the 3 mg. division of the beam to the 4 mg. division will shift the rest point 4.0 scale divisions to the left at this load. By moving the rider $\frac{2.0 - 0.5}{4.0} = \frac{1.5}{4.0} = 0.38$ large (milligram) divisions, the original position of equilibrium of the beam will be restored. Since 0.38 large beam division $\equiv$ 0.38 mg., the weight of the object is $14.53000 + 0.00300 + 0.00038 = 14.53338$ g. (In ordinary analytical weighings this value would be rounded off to the fourth decimal place: 14.5334 g.)

Alternative method of obtaining the tenths of a mg. Instead of *calculating* the point at which the rider should be placed to make the zero point and rest point coincide, the rider may be moved along the beam until a point is found at which the original position of the beam is restored. This is the method usually employed in quantitative work in which weighings need not be made with an accuracy greater than 0.1 mg. In this method the sensitivity of the balance need not be known. If, however, the sensitivity is approximately known (as it should be), it is possible to determine by mental calculation the point at which the rider should be placed, when the balance is nearly in equilibrium, to make the rest point coincide with the zero point. The rider is then placed at this point, and the correctness of the position is verified by observation of swings. If the two points agree within ¼ of a division, then the weight of the object has been found to within approximately 0.05 mg. if the sensitivity of the balance is 4 or more divisions per milligram. In ordinary quantitative work weighings are made to the nearest 0.1 mg. only.

When it is not necessary to determine the zero point. If a substance is weighed by difference at one sitting, it is not necessary to find the zero point of the balance. In such a case it is permissible to assume that the zero point lies at the center of the scale, and the weight of the container + substance is found on this assumption. The substance, or a part of it, is poured out and the weight of the container found by adding weights until the rest point lies at the center of the scale again. The difference between the zero point and the rest point in both weighings will be the same, provided that the zero point has not shifted during the weighing, and therefore need not be known. It is not likely that the zero point will change a detectable amount during the weighing if the interval between the first and second weighings is small, i.e., a few minutes. In weighing out a sample this method may be used, the zero point being assumed to lie at any convenient point on the scale, usually at the center. If there is a possibility that the zero point will change between weighings, then this method may not be used. For example, if the weight of an ignited residue is to be obtained, it is not permissible to weigh the empty crucible assuming the zero point to lie at the zero of the scale, then to place the precipitate in the crucible and to make the ignition, and finally to reweigh, adjusting the weights until the rest point lies at the center of the scale. During the time required for the ignition and cooling of the crucible, there is a possibility that the zero point of the instrument has changed, especially if the balance has been used in the meantime.

2. ***The method of short swings.***[1] For ordinary analytical weighings in which it is not necessary to weigh with an accuracy greater than 0.1 mg., the method of short swings may be used. Indeed, this method can often be employed for making weighings to 0.02 mg. In this method the zero or rest point is found by adding the observed values of two successive short swings — one on each side of the center mark — and dividing by two to obtain the mean value. This mean value — indicating the center of the swing — will give the equilibrium point of the balance if the swings are short. The method is based upon the fact that if the swings are short enough the decrease in amplitude of each swing due to the resistance of the air and friction in the bearings will be so small that it will be inappreciable, and it is then permissible to take the mean of two successive end points of a swing as the zero point. Thus, in the example given in the preceding section, the zero point as determined by this method from the first two readings on either side of the center is $\frac{-4.2 + 4.4}{2} = +0.1$. It will be seen that the deviation from the true zero point (+ 0.15) is so small as to be entirely negligible in a balance having the usual sensitivity of 3 to 4 divisions per milligram. The difference could be made smaller by using swings shorter than 4 divisions. Thus, if a swing of 2 divisions were used, the decrease in amplitude with each swing would be approximately one half of what it is at 4 divisions, since the retardation is approximately proportional to the amplitude.

---

[1] H. L. Wells, J. Am. Chem. Soc. 42, 411 (1920).

Furthermore, any error made in determining the zero point in this manner would be compensated in the weighing if the amplitude were approximately the same in both cases and the swing were read in the same direction each time, e.g., from right to left. The length of the swings for use in this method may vary from 1 to 4 divisions.

It is recommended that this method of weighing be used in preference to the more elaborate one involving the determination of the zero or rest point from several swings. The latter method requires much more time, and the accuracy is probably no greater in the majority of cases. When a sample is weighed out by the method of short swings, the container and substance is counterbalanced with weights until the pointer swings equal short distances — say, 1 or 2 divisions — on both sides of the center mark of the scale; the sample is then poured out and the weights adjusted until the pointer again swings equal distances on both sides.

For the calibration of weights, in which the results must be of the highest accuracy, the method of swings should be used.

3. ***The single-deflection method.***[1] One arm of the balance to be used for this method of weighing is made permanently heavier than the other, so that when the beam is lowered and the pans released the pointer will swing over a number of divisions to one side. The limit of the swing is taken as representing the zero point of the instrument. The weight of an object is obtained by adding weights until the pointer swings out the same number of divisions as before.

It is highly important that the pan supports be so adjusted that no impulse is delivered to the pans when they are released. The method cannot be used on balances that have a combined beam and pan-arrest mechanism. One side of the beam is made heavier than the other by turning the adjusting nut at the end of one of the arms. Usually the left-hand side is made heavier so that the pointer will swing to the right. If it is desired not to disturb the adjustment of the balance, a milligram weight or any other light object is placed on the left pan. The distance that the pointer swings out should preferably lie in the range 3–6 divisions. The pans should be released smoothly and not too slowly when using this method. If the pan-arrest button is pushed in too slowly, there is danger that the pointer will give swings of variable length. Before this method is used, the balance should be carefully tested to see whether consistent results can be obtained with it. When the pan supports are properly adjusted, a balance will give very constant deflections. A balance having a sensitivity of 1 mg. ≡ 4.0 divisions of scale was found to give deflections differing at the most by only 0.1 division — the probable error of estimating the tenths of a division.

---

[1] P. H. M.-P. Brinton, J. Am. Chem. Soc. *41*, 1151 (1919).

It should not be forgotten when this method is used that the length of the deflection depends upon the sensitivity and, therefore, upon the load on the balance. When large amounts of material or a heavy object is to be weighed with great accuracy, the sensitivity, or the length of swing at different loads for the same overweight, must be determined. Usually this is not necessary because most analytical weighings involve obtaining the difference between two weights, and this difference is always small (ordinarily less than a gram) so that the change in sensitivity for this small change in load is inappreciable. On the other hand, if a large amount of substance is weighed, the *percentage* error due to change in sensitivity will be very small and can in most cases be neglected.

The single-deflection method of weighing can be used to advantage in the weighing of very hygroscopic substances. The weight of the ignited residue, for example, is first found approximately to a milligram; and then, after heating and cooling, the crucible is placed on the balance and the deflection read. From the length of the swing of the empty balance and the sensitivity at the load in question, the true weight of the crucible and its contents is obtained by a simple calculation in a manner analogous to that described under the method of swings. The weighing takes such a short time that no sensible increase in weight due to absorption of moisture occurs.

4. ***The microchemical method.*** It is customary in weighing with the microchemical balance to call the tenths of a pointer division units and to represent the zero or rest point by the *deflection sum.* For example, if the successive pointer readings are 1.8 (left of zero), 2.8 (right), and 1.6 (left), the zero point by this method would be $-(18 + 16)\frac{1}{2} + 28 = 11$. This method can of course be used in weighing with the ordinary analytical balance.

Inequality of length of balance arms.

The direct method of weighing will give the true mass of the object only if the two arms of the beam have the same length (and the weighings are made *in vacuo*). If the right arm is slightly longer than the left and the object is placed on the left pan, it is evident that the direct weighing will assign a mass to the object which is a trifle less than the true value, the deviation depending upon the ratio of the arm lengths. In a good analytical balance the arms will seldom differ in length by more than one part in 50,000. If an *absolute* weight must be determined with an accuracy greater than that corresponding to the difference in the length of the arms, it will be necessary to weigh by the method of transposition or substitution, to be described in the next section.

In the determination of the percentage of a constituent in a substance, it is not at all necessary to determine absolute weights. If the sample and the ignited or dried residue are both weighed on the same balance, and on the same pan, it is clear that the percentage of the constituent sought will not be affected by the difference in length of the balance arms, because the weights of sample and residue are altered in the same proportion:[1]

---

[1] This is based on the assumption that the ratio of the arm lengths always remains the same, which is generally the case. If one arm should be heated slightly more than the other or if by rough handling a knife-edge should be shifted, it would no longer be true, of course.

$$\text{Percentage of constituent} = \frac{\text{True weight of constituent}}{\text{True weight of sample}} \times 100$$

$$= \frac{\text{Apparent weight of constituent}}{\text{Apparent weight of sample}} \times \frac{\frac{L_r}{L_l}}{\frac{L_r}{L_l}} \times 100$$

$$= \frac{\text{Apparent weight of constituent}}{\text{Apparent weight of sample}} \times 100$$

where L_l = length of left-hand balance arm
L_r = length of right-hand balance arm.

(Apparent weights refer to *vacuo* weights.)

Whenever the value of a *ratio* is to be obtained, apparent weights may be used in place of absolute or true weights. However, objects to be weighed must then always be placed on the same pan on the same balance.

It is sometimes necessary to find the true weight of an object. True weights, for example, are desirable or required in the calibration of weights, in the calibration of volumetric apparatus (p. 524), and in other cases not so frequently encountered. In the calibration of weights the true mass of a weight may have to be determined with an accuracy of one part in one million, or even better. Since it is a mechanical impossibility in manufacture to set the agate knife-edges in the beam so that the difference in the lengths of the arms will be this small, it is absolutely necessary to take the inequality into account. In the calibration of volumetric apparatus the difference in length of the arms can be neglected if the weighing can be made on an analytical balance. When a half-liter or a liter flask is to be calibrated by weighing out an absolute amount of water, an analytical balance cannot be used; a rougher balance of greater capacity must then be employed, and since in such a balance the arm lengths may be quite different, it is necessary to avoid this possible error by weighing by one of the methods described in the next section.

Weighing by transposition (double weighing; method of Gauss).

In this method the object is weighed first on one pan and then on the other. The mass of the object is the square root of the product of the weights required to counterbalance it in the two cases.

Let L_l = length of left arm
L_r = length of right arm
M_o = mass of object (i.e., true mass)
W_l = mass of weights on left pan required to counterbalance object = apparent mass of object placed on right pan
W_r = mass of weights on right pan required to counterbalance object = apparent mass of object placed on left pan.

At equilibrium, when the object is on the left pan, it follows from the principle of moments that

$$M_oL_l = W_rL_r \tag{1}$$

and when the object is placed on the right pan that

$$M_oL_r = W_lL_l. \tag{2}$$

Multiplying (1) by (2), $M_o^2L_lL_r = W_lW_rL_lL_r$

or

$$M_o^2 = W_lW_r$$

$$\therefore M_o = \sqrt{W_lW_r}.$$

Since W_l and W_r are very nearly equal, it is permissible to write:[1]

$$M_o = \frac{W_l + W_r}{2}.$$

It is assumed that no corrections need be applied for air buoyancy.

Ratio of lengths of balance arms. By dividing equation (2) by equation (1) and solving for $\frac{L_l}{L_r}$, the following expression is obtained:

$$\frac{L_l}{L_r} = \sqrt{\frac{W_r}{W_l}}.$$

By means of this equation it is easy to calculate the ratio of the balance-arm lengths at the time the weighing was made with the load M_o on the pans. It should be realized that $\frac{L_l}{L_r}$ is not a constant but a value that varies depending upon conditions. If one arm should be warmed slightly more than the other, then the ratio would be changed. Even if both arms are heated equally, one may expand slightly more than the other, for although both arms are of the same material it is not necessarily true that each arm has the same coefficient of expansion.[2] Furthermore, the value of the ratio may vary with the load upon the pans and may depend upon other factors. Therefore, the ratio of arm lengths determined for one set of conditions may not be used for the calculation of the true mass of an object weighed under different conditions, except when an approximation is desired.

Weighing by substitution (method of Borda).

This is another method used for finding the true mass of an object, irrespective of differences in arm lengths. The object is placed on the right-hand pan and counterbalanced with another body of about the same weight, called a *tare.* The rest point of the balance is determined, and the object is then removed and replaced by weights which give the same rest point. The mass of the object is then equal to the mass of the weights (leaving out of consideration for the time being the buoyancy effect of the air), since both object and weights have been acting through the same arm length, L_r.

The precision attainable by this method is but half of that attainable by the method of transposition. Therefore the latter method should be used when the true mass of a body must be determined with utmost precision.

ERRORS IN WEIGHING

The chief sources of error are the following:[3]

1. Inequality of the length of the balance arms when the direct method of weighing is used.

---

[1] If the difference between W_l and $W_r = d$, the percentage error introduced by this approximation is equal to $100\left(\frac{d}{L}\right)^2$.

[2] The coefficient of thermal expansion of a solid depends somewhat upon its physical condition, and the two arms of a balance may not be exactly similar in physical properties.

[3] Not necessarily arranged in the order of importance.

2. Errors resulting from change of condition of the substance or the vessel in which it is weighed.
3. Buoyant effect of air.
4. Inaccuracy of weights (a common source of error)

We do not consider here such apparent sources of error as change in the zero point of the balance, unequal heating of the beam, stray air currents, etc., all of which can be avoided very easily by a little care.

The first source of error — inequality of balance arms — we have already sufficiently discussed. In succeeding sections the other sources of error will be considered.

Errors due to buoyancy of air.

It is a well-known principle of physics that a body immersed in a fluid, i.e., either a liquid or a gas, is buoyed up by a force equal to the weight of the fluid displaced. However, no error would be introduced from this cause in weighing if the weights used to counterbalance the object would lose exactly as much in weight as the object itself. But this is generally not the case, because the density of the weights is usually different from that of the object, and consequently the volume of air displaced by the two will be different. If the density of the weights is greater than the density of the object weighed (the usual case in quantitative analysis), the latter will displace a greater volume of air than the former and will weigh a little less in air than in vacuum.

First, let us inquire into the magnitude of the error. Suppose sodium chloride is being weighed with brass weights in air at 20°, the atmospheric pressure being 760 mm. The density[1] of sodium chloride is 2.13, that of brass[2] is 8.4. One ml. of dry air at 20° and 760 mm. pressure weighs 0.00120 g. Therefore the apparent loss in weight of 1 g. of sodium chloride will be $\frac{0.00120}{2.13} = 0.00056$ g., and that of 1 g. of brass will be $\frac{0.00120}{8.4} = 0.00014$ g. Therefore one gram of sodium chloride will weigh $0.00056 - 0.00014 = 0.00042$ g. less in air than *in vacuo*, a difference of -0.04 per cent. In the same manner the loss in weight of any substance weighed in air can be calculated if its density and the density of the air at the time of weighing are known. Conversely, the vacuum or true weight of a body can be calculated from its apparent weight in air if its density is known. The true weight of an amount of sodium chloride weighing 1.0000 g.

---

[1] Density is defined as mass per unit volume. In the c.g.s. system density is expressed in terms of g./ml.

[2] The density of brass depends upon its composition. Brass used for the manufacture of weights may be taken to have the density 8.4. In very accurate work the density of the particular weights used must be determined.

in air at standard conditions is 1.0004 g. The following relation holds between the true weight of a body and its apparent weight in air:[1]

$$W = W_A + d_A\left(\frac{W_A}{d} - \frac{W_A}{d_W}\right)$$

where W = true (vacuum) weight of the body
W_A = apparent weight of the body in air = mass of the weights
d_A = density (g./ml.) of air at time of weighing (depends upon pressure, temperature, and humidity of atmosphere)
d = density of the body
d_W = density of the weights.

The closer the density of the body weighed approaches the density of the weights used, the smaller the difference between true and apparent weights becomes, until when the two are equal the weight in air is also the true weight. If the body has a density greater than the weights, then its apparent weight in air will be greater than the true weight.

The buoyant effect of the air will not necessarily introduce an appreciable error into a determination. It must be remembered that most analytical results are stated in the form of a ratio:

$$\text{Percentage of constituent} = \frac{\text{Weight of constituent}}{\text{Weight of sample}} \times 100$$

Now if the density of the weighing form of the constituent is equal, or nearly equal, to that of the sample, it is evident that no appreciable error can result from using apparent weights in air for the calculation of percentage. Only in those cases in which the densities of the two are quite different, will it be necessary to correct the air weights to true weights. In most instances the densities of the two differ relatively little, and it is unnecessary in ordinary careful analytical work to reduce weights to *vacuo*. A rather unfavorable case may be taken for illustration. Soluble chlorides are determined by precipitating with silver nitrate to give silver chloride, which is weighed after drying. The density of silver chloride, 5.6, is very different from that of an alkali chloride, say sodium chloride ($d = 2.1$). In the following table are given the percentage corrections to be added (algebraically) to the air weights of sodium chloride and silver chloride (obtained with weights of various materials) to obtain the true weights in vacuum:

SUBSTANCE	CORRECTION %		
	Aluminum Weights (d = 2.65)	Brass Weights (d = 8.4)	Platinum Weights (d = 21.5)
Silver chloride	− 0.024	+ 0.007	+ 0.017
Sodium chloride	+ 0.012	+ 0.043	+ 0.053
Difference	− 0.036	− 0.036	− 0.036

---

[1] Strictly $W = W_A + d_A\left(\frac{W}{d} - \frac{W_A}{d_W}\right)$ but since W is very nearly equal to W_A it may be replaced by the latter in the case of solids and liquids.

The percentage of chloride in a sample is calculated from a formula of the form:

$$\frac{\text{Weight of silver chloride} \times \text{factor} \times 100}{\text{Weight of sample}},$$

in which the true weights of the substances are written. If air weights are used, it is evident that the true weight of chlorine can be found by applying the corrections found above. Thus, suppose that the percentage of chlorine in a sample of impure sodium chloride calculated from air weights is found to be 60.02. The true percentage will be $60.02 \times \frac{1 - 0.00024}{1 + 0.00012}$ if aluminum weights were used for weighing. This value is equivalent to $60.02 - (60.02 \times 0.00036) = 60.02 - 0.022 = 60.00$ per cent. The correction difference is, of course, independent of the material of the weights, provided that both the sample and the precipitate obtained from it are weighed with the same kind of weights. It will be seen that the difference between the true and apparent percentages is small in this case, amounting to 0.036 or 0.04 per cent. In most determinations the difference would be even smaller. In ordinary careful analytical work it is usually justifiable to neglect the air corrections, since an accuracy better than 0.1 per cent, i.e., one part per thousand, is not sought nor easily attainable. In more precise work, for example in testing the accuracy of a method and especially in atomic-weight determinations, it is necessary to take the corrections into account. When standard substances are intercompared, weights must be corrected to *vacuo*. The difference in titer of an acid solution standardized against borax ($d = 1.7$) and sodium carbonate ($d = 2.5$) amounts to 0.02 per cent when vacuum corrections are not made.

When absolute weights are desired, it is important to apply vacuum corrections. One important case of this nature arises in analytical work, namely, the calibration of volumetric glassware by weighing out water. Since the density of water is accurately known at any temperature, it is easy to weigh out an amount of water that will indicate a certain desired volume (p. 525). It is highly important to correct for the buoyancy of the air in such work. If this correction should not be applied, the error made will amount to $0.0012 \left(1 - \frac{1}{8.4}\right) \times 100$ per cent $= 0.106$ per cent, if the weighings are made, as they always are, with brass weights. This error would amount to slightly more than 1 ml. in the calibration of a liter volumetric flask and is too large to neglect.

In the determination of atomic weights the vacuum corrections must be determined with great exactness. The density of the air at the time of the weighing must either be determined,[1] or calculated from its temperature, the atmospheric pressure, the humidity, and the value of gravity; all of these factors affect the density, and therefore the mass, of the air displaced by the object.[2]

For laboratories situated below an altitude of 1000 feet, the density of the air will rarely fall outside the limits, 0.0011 and 0.0013 g./ml.; and it is permissible for *analytical purposes* to use the average value, 0.0012, in the calculations when vacuum corrections must be applied.

---

[1] G. P. Baxter, J. Am. Chem. Soc. *43*, 1317 (1921).

[2] It is also possible to avoid buoyancy errors by actually carrying out the weighings *in vacuo*. Theoretically, this is the best procedure, but it presents a number of practical difficulties so that it is rarely used even in atomic-weight work.

Avoiding the error due to air buoyancy by the use of rational atomic weights. A device for avoiding or, more properly expressed, reducing the errors resulting from air buoyancy in weighing is the use of the so-called rational atomic weights.[1] The principle here involved may perhaps best be brought out by an example. In calculating the percentage of chlorine in a chloride, using the customary gravimetric method of weighing precipitated silver chloride after drying, the formula employed is:

$$\frac{\text{Weight of silver chloride} \times \dfrac{\text{Cl}}{\text{AgCl}} \times 100}{\text{Weight of sample}}$$

Since in this formula *weight* refers to vacuum weight, both the air weight of the sample and that of the silver chloride must be reduced to *vacuo* by the method described above; and then the value of the ratio $\frac{\text{Cl}}{\text{AgCl}}$ calculated from the international atomic weights can be introduced in the expression. The international atomic weights are, of course, based upon weighings *in vacuo,* and therefore the weight of chlorine thus found is the vacuum weight. Now it is possible to proceed in a converse manner to find the value of the percentage of chlorine in the sample from air weighings. Suppose we can find the air weight of the true amount of chlorine in the sample of given air weight. Then the true percentage of chlorine can be calculated. Actually it is possible to do this by using what may be called air-atomic weights, i.e., atomic weights that have been corrected for the buoyancy of the air. These are the *rational atomic weights.* Rational atomic weights may be used in computing rational molecular weights, the atomic volumes being additive within limits. The rational atomic weights are not calculated from the atomic volumes of the elements themselves but from the average values which they have in various compounds. The calculations have been based on the assumption of the use of brass weights[2] (density = 8.4) and weighing in air under standard conditions (0°, 760 mm. pressure).

---

[1] N. Schoorl, Z. anal. Chem. 57, 209 (1918).

[2] The use of other weights introduces no error if they have been adjusted against brass in air, which is generally the case.

Returning now to the example, it will be seen that by using the rational atomic weights in the factor $\frac{Cl}{AgCl}$, we obtain the weight of chlorine under the same conditions as the weight of the sample, and thereby the correct percentage of chlorine, provided the atomic volumes of the elements concerned are the same as those upon which the table of rational atomic weights has been constructed. It will be seen that this method of correcting for the buoyancy of the air has the advantage of rapidity and does not require a knowledge of the density of the weighing form and the sample itself. Unfortunately, great accuracy cannot be attained in this method, because the atomic volumes of the elements vary to a considerable extent in their various compounds[1] and the values of the rational atomic weights in the table are necessarily average values. As already mentioned, the use of the rational atomic weights is based upon weighing in air under standard conditions, and therefore change in the density of the air due to variation in temperature and pressure is not taken into account. The error due to the latter deviations is so small in ordinary cases that it hardly enters into consideration in even refined analytical work (excluding, of course, atomic-weight determinations).

In spite of these objections, the use of the rational atomic weights is preferable to that of the international atomic weights in ordinary analytical work in those cases in which air buoyancy introduces an appreciable error. In any case the results obtained by using the rational atomic weights in the calculations will be at least as accurate as those obtained with the international; and even when the error due to deviation of the atomic volumes from the average is pronounced, the results will be better, although perhaps not sufficiently accurate for the purpose. Even if they served no other purpose, the rational atomic weights would provide a rapid means of obtaining the magnitude of the error due to the buoyancy of the air in any determination, thus serving to indicate whether a correction is necessary.

It is emphasized that the international atomic weights are fundamental constants and that the rational atomic weights simply provide a means of eliminating, to some extent at least, the errors resulting from air buoyancy in practical analysis.

Changes in weight or condition of a substance or container during weighing.

1. *Adsorption of moisture.* It is a general fact that any material placed in a moist atmosphere will adsorb water at its surface, thus increasing its weight (p. 132). The amount of water adsorbed depends in the first place upon the properties of the material itself: extent of surface and especially the adsorptive powers of the substance, and, secondly, upon the relative humidity and temperature of the atmosphere in which it is placed. A material can be freed of its surface water by heating to a high temperature. After cooling, it can be kept moisture-free by placing it in a desiccator containing a suitable drying agent. When the dried material is placed in the balance pan, it will adsorb or absorb more or less moisture from the air, and an increase of weight may be noticed during the weighing. Porcelain and platinum crucibles are so very

---

[1] In the case of calcium, for example, the atomic volumes of the element in various compounds are as follows: Ca (metal) 26, CaO 11, $CaCl_2$ 20, $CaBr_2$ 18, CaI_2 11, $CaSO_4$ 6.

slightly hygroscopic that the increase in weight of crucibles that have been heated and cooled will usually be inappreciable in the few minutes required to make a weighing. On the other hand, large objects of glass may increase sensibly in weight during the weighing if they are moisture-free to start with. Since the adsorption of moisture may be slow, it is recommendable to wipe the container with a damp lintless cloth to saturate the surface with water, then with a dry cloth to remove the excess moisture, and finally to let it stand in the balance until the weight is constant. This procedure, which is used when the container cannot be heated to a high temperature, is based upon the fact that a surface containing an amount of water greater than the equilibrium concentration will come to equilibrium sooner than one which contains less than the required amount. The best method, however, for eliminating errors due to adsorption of water on surfaces of vessels is the use of a *tare*, a vessel which is as much like the vessel to be weighed as possible, both in weight and surface exposed. The tare is exposed to the same influences as the vessel itself during the determination and is used to counterbalance the latter before and after any treatment to which it may be subjected. In this way errors arising from adsorption of moisture by the container are canceled. Errors resulting from a change in humidity between the two weighings are eliminated.

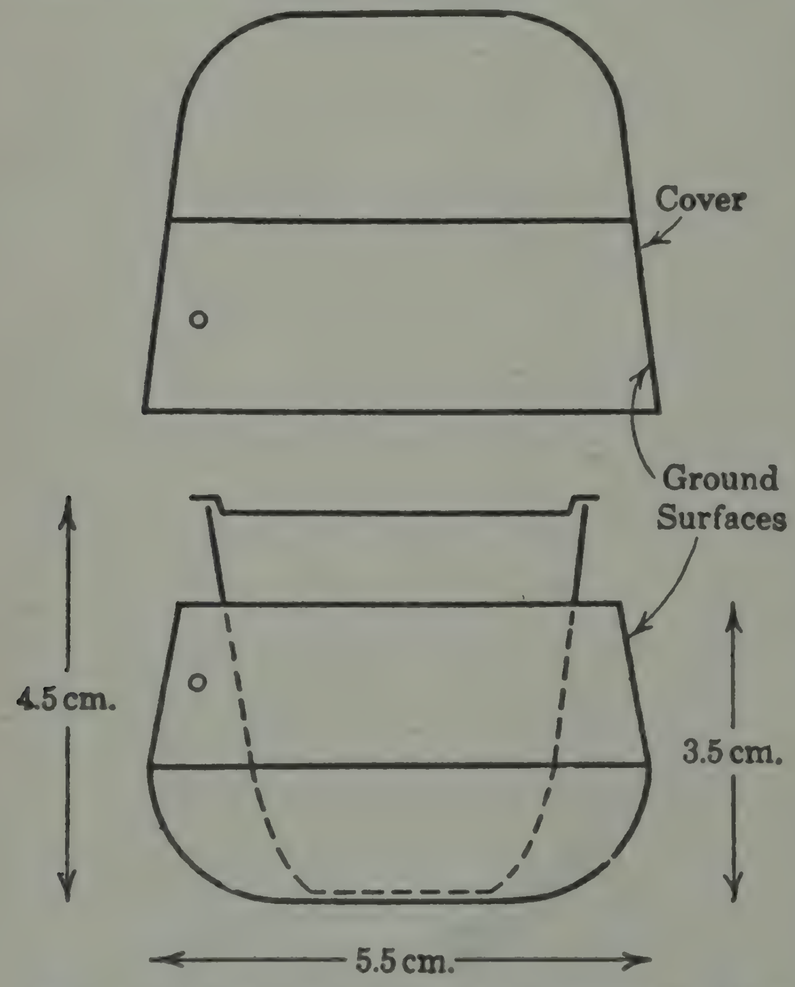


FIG. 51. Weighing bottle for crucibles. (Redrawn from Hoffman and Lundell, J. Res. Natl. Bur. Standards *18*, 1 (1937).)

The adsorption of moisture by a substance to be weighed is usually much more serious than adsorption by a container. The substance may be very hygroscopic by nature, or on account of its great surface development it may adsorb large amounts of water when it would not do so in a compact form. Nearly all finely divided precipitates are sensibly hygroscopic, and precautions must be taken in weighing them. If the substance is only slightly hygroscopic, it may often be weighed with sufficient accuracy by carrying out the operation rapidly, the container being covered or closed as well as possible. Even markedly hygroscopic materials may be weighed with accuracy if the weights are on the pan, and the rider or chain is nearly adjusted as indicated by a preliminary approximate weighing. When the container and its contents are placed on the pan the second time after heating and cooling, the rest point can be found from two swings or, still better, from a single deflection, and the true weight calculated from the zero point of the empty balance and the sensitivity. If a crucible is thus being weighed, it should be kept covered at all times. If a substance can be weighed in a weighing bottle, it is best to use this, for such a container can be tightly closed. An unusually hygroscopic substance contained in a crucible can be weighed by placing the crucible in a large closed weighing bottle and weighing the latter against a similar bottle used as a tare (Fig. 51). This procedure, however, rarely needs to be adopted.

2. *Electrification of containers.* Electrification of glass containers may have to be guarded against. Dry glass vessels if rubbed with a cloth may acquire a considerable charge of static electricity, and such objects placed on the balance will show an erroneous weight on account of the attraction of the charged container for the walls or floor of the balance. The effect is most noticeable when the atmosphere has low humidity (< 40 per cent).[1] Pyrex is more easily electrified by friction than ordinary glass, and quartz more easily than Pyrex. The charge can be dissipated by exposing the vessel to ultraviolet light[2] or a high-frequency electrical discharge.[3]

3. *Differences in temperature of container and balance.* It is highly important that the object weighed have the same temperature as the balance; if there is a temperature difference, serious errors may be made.[4] If the object has a temperature slightly higher than that of the balance, its apparent weight will be less than its true weight for either or both of two reasons. In the first place, the body will be buoyed up by convection currents set up by itself; then, if the body be cavernous, especially if it is closed, the air within it may have a slightly lower density than the air in the balance case, and therefore its weight will appear to be slightly less than it really is. The magnitude of the latter error is readily calculated. Suppose a 25 ml. *covered* crucible having a temperature of 26° is weighed in a balance in which the air temperature is 25°. Assuming that the air at a temperature of 25° has a density of 0.00120, the weight of the air in the crucible — temperature = 26° — will be $25 \times 0.00120 \times \frac{298}{299} = 0.0299$ g., whereas if the temperature of the air in the crucible were 25°, the weight would be 0.0300. The difference involved, $0.0300 - 0.0299 = 0.0001$ g., makes itself known as a buoyant force on the crucible. In this particular case a difference in temperature of crucible and balance of only 1° causes an error of 0.1 mg. If the crucible were uncovered, the error from this source would become smaller owing to the replacement of the warm air by colder air. Crucibles carelessly cooled may have apparent weights that are much too small, especially if covered, as crucibles containing precipitates should be during weighing. There is also danger that the ratio of the length of the balance arms will be changed if a warm object is weighed.

The length of time a crucible should be cooled in a desiccator before weighing cannot be exactly specified, since it depends upon the size and temperature of the crucible as well as the material of which it is composed. Porcelain crucibles must be kept in a desiccator longer than platinum crucibles. In general, porcelain crucibles should be cooled for one-half hour before weighing.

---

[1] D. F. Hayman, Ind. Eng. Chem., Anal. Ed. *8*, 343 (1936), states that electrification does not take place above a relative humidity of 45 per cent.

[2] C. J. Rodden, Ind. Eng. Chem., Anal. Ed. *12*, 693 (1940).

[3] F. W. Van Straten and W. F. Ehret, *ibid.* *9*, 443 (1937).

[4] For an experimental study of the differential temperature error in weighing see E. Blade, Ind. Eng. Chem., Anal. Ed. *12*, 330 (1940).

When weighing out samples from weighing bottles, care should be taken not to heat these by excessive handling with the fingers, for the heating of the air in the bottles may lead to very appreciable errors as already shown. If the container is held lightly with the finger tips for only a short time, no serious error will result, although grasping the bottle with a folded strip of filter paper is to be preferred.

CALIBRATION OF WEIGHTS

For most purposes of quantitative analysis it is not necessary to know the absolute values of the weights used, because most analytical results are derived from ratios of weights; and, as we have already shown, it is not then necessary to express the weights in terms of absolute values. However, even if the numbers on the weights do not indicate the actual weights, it is essential that the weights agree among themselves; i.e., the 20 mg. weight must have exactly twice the mass [1] of the 10 mg., the 50 mg. weight must be five times as heavy as the 10 mg., and so on. If the weights agree among themselves in this way to 0.1 mg. in each case, they are suitable for use in quantitative weighings. In the manufacture of weights it is difficult to make a weight correspond exactly to its face value without expending a great deal of labor upon the adjustment. An accurately adjusted set of weights is expensive. A moderately priced set of weights, such as the student is likely to use in his weighings, has not, in general, been adjusted with such care that each piece can be relied upon to 0.1 mg.; and for that matter no set of weights, no matter how expensive, can be absolutely trusted. For this reason it is necessary to *calibrate* or *standardize* a set of weights before using it in quantitative work. Even if the weights are accurate to within 0.1 mg. when new, it is advisable to calibrate them at regular intervals when they are in steady use, because changes may occur due to wear, corrosion, or other causes.

The method of calibration to be described is that of Richards.[2] The principle of the method is this: The 5 (or 10) mg. weight is first arbitrarily assigned the value of 5.00 mg. (or 10 mg.), and the relative masses of all the other weights are determined and expressed in terms of the 5 mg. weight chosen as standard. First, the 5 mg. weight is compared with the 5 mg. rider, then the 5 mg. weight plus the rider with the 10 mg. weight, and so on. The values for the larger weights obtained by this method will differ considerably from the nominal values because such a small standard is used. It is, therefore, customary to assume that one of the large weights, say the 10 g., weighs 10.00000 g. and to express the weights of all the other pieces in terms of the 10 g. weight. If the absolute value of the 10 g. weight, or any other large weight, is determined by comparison with a weight of known mass (a standard weight), it is a simple matter to calculate the absolute values of all the other weights, since the ratios of the 10 g. weight to the others have been determined.

Weighings in calibrations are made either by substitution or transposition. Weighing by substitution requires another set of weights, the pieces of which serve as tares; of course, these pieces need not be accurate. The accuracy obtainable by the method of transposition is twice as great as that by substitution.

---

[1] In this section we employ the term *mass* with the reservation that it may include the denotation *apparent mass in air*.

[2] T. W. Richards, J. Am. Chem. Soc. *22*, 144 (1900).

The ideal method of calibration would consist of the direct comparison of each weight with a standard weight of the same denomination.

Calibration of weights according to Richards.[1]

1. *Calibration of weights using the substitution method of weighing.* Before the calibration is begun, it is necessary to see that duplicate and triplicate weights are marked so that they can be readily distinguished. Duplicates can be differentiated by marking with one or two dots imprinted with a punch. Such marking of weights should never be done by the student but should be referred to an experienced person.

First of all the rider is compared with a weight of the same mass. If the beam is graduated into five large divisions and carries a 5 mg. rider, then the latter is compared with the 5 mg. weight. If the rider weighs 10 mg., the comparison is made against the 10 mg. weight. We will suppose that the balance takes a 10 mg. rider. The 10 mg. weight from the auxiliary set which is to serve as a tare is placed on the left balance pan, and the rider is placed *exactly* on the 10 mg. mark on the right arm of the beam. The rest point of the balance is now found by the precise method of swings, the calculations being carried to the nearest 0.05 of a division.[2] The rider is removed from the beam, one of the 10 mg. weights is placed on the right pan, and the rest point of the balance is found for this weight. From the known sensitivity of the balance, the difference in weight between the rider and the 10 mg. weight is calculated, it being assumed that the 10 mg. weight is correct. In the same manner the following comparisons of weights are made:[3]

0.01″ g. against 0.01′ g.
0.02 " 0.01′ + 0.01″
0.05 " Σ0.05 (0.02 + 0.01′ + 0.01″ + rider at 10 mg.)
0.1′ " Σ0.1
0.1″ " 0.1′
0.2 " 0.1′ + 0.1″
0.5 " Σ0.5
1′ " Σ1
1″ " 1′
1‴ " 1′
2 " 1′ + 1″
5 " 2 + 1′ + 1″ + 1‴
10′ " 5 + 2 + 1′ + 1″ + 1‴
10″ " 10′
20 " 10′ + 10″
50 " 20 + 10′ + 10″ + 5 + 2 + 1′ + 1″ + 1‴.

---

[1] For an examination of the rationale of Richards' method of weight calibration, see E. Blade, Ind. Eng. Chem., Anal. Ed. *11*, 499 (1939); F. H. Hurley, Jr., *ibid.* *9*, 239 (1937); F. C. Eaton, J. Am. Chem. Soc. *54*, 3261 (1932).

[2] The sensitivity of the balance should be at least 1 mg. ≡ 3 scale divisions, and preferably 1 mg. ≡ 5 divisions.

[3] In the case of a chainomatic balance the chain should be calibrated at 10 mg. intervals, or less preferably at the end of its range only.

The data are recorded systematically, as in Table XL. Calculations are made to the nearest 0.01 mg.

Explanation of Table XL and method of calculation of corrections. The first column, headed T, gives the denomination of the tare placed on the left-hand pan. The second column contains the denomination of the weight being compared with the tare; (W) indicates the nominal weight of the piece in grams. The rest point obtained in each weighing is recorded in the next column, headed R. The next column, S, gives the sensitivity of the balance at various loads; the figures denote the number of scale divisions that the rest point of the balance is shifted by an excess weight of 1 mg.[1] In the fifth column, headed d, the difference in weight, expressed in milligrams, between the weight in question and the preceding weight or sum of weights is recorded. The difference is calculated from the expression $\frac{R_1 - R_2}{S}$, where R_1 is the rest point given by the preceding weight, and R_2 is the rest point with the weight in question, the mass of which is to be expressed in terms of the preceding, and S is the sensitivity for the load on the pans. If R_1 is greater than R_2, the difference, d, will be positive, which means that the mass of (W) is greater than that of the preceding weight or sum of weights. In the column headed $W_{0.01}$ the mass of (W) is expressed in terms of the mass of the 0.01′ g. weight, i.e., the assumption is made that the latter has a mass of 0.01000 g.; and the mass of (W) is calculated from the preceding successive weights on this basis from the values of d. The values thus obtained will differ considerably from the face values of the weights, as already stated, because the standard chosen is so small. It is therefore convenient, after having obtained the relative masses of the weights, to express the masses in terms of a standard having a larger mass. There are two ways of proceeding:

1. It may be assumed that one of the larger weights, e.g., the 10′ g. weight, has a mass exactly equal to its nominal value, i.e., 10.00000 g.; and then one can calculate the masses of the other weights on this basis. From the new series of values thus obtained, a set of corrections is derived,

---

[1] It may be pointed out that it is assumed the rider has a mass which is close to 5 or 10 mg., as the case may be, or at least does not differ much from the 5 or 10 mg. weight which is made the basis of the series of relative weight values. If this assumption does not hold, the values for the sensitivity, S, will be in error, i.e., not consistent with the weights based on the 5 or 10 mg. weight. The result of the comparison between the rider and the 5 or 10 mg. weight (the second observation in Table XL) tells us at once whether the assumption is justified. A difference of 0.2 or 0.3 mg. with a 10 mg. rider does not lead to any serious error in the value of S so far as an ordinary weight calibration is concerned. However, it is desirable that the rider and the 5 or 10 mg. weight have the same mass within the experimental error of weighing so that it will not be necessary to apply a correction for different positions of the rider on the beam. All difficulties can be avoided by making the rider the standard and finding the masses of all the weights in terms of it (Hurley, *loc. cit.*).

One other assumption is involved in the procedure described above, namely, that when the rider is placed, for example, on the 1 mg. mark, it has an effective weight equal to 1/5 or 1/10 of its actual weight, or in other words that the beam is accurately graduated. This possible error need not cause much concern. It would be a bad analytical balance indeed that would have an error of 1 or 2 per cent in its beam markings.

and these corrections are applied to all weighings made with the set in which a ratio of weights is determined. It should be emphasized again that in most analytical processes the ratio of two weights and not an absolute weight is required. As long as only the value of a ratio is to be determined, any weight in the set can be arbitrarily assumed to be correct; and the masses of the other weights can be derived on this basis from the experimentally determined relative weights, $W_{0.01}$.

2. Any *large* piece in the set may be compared with a standard weight of the same denomination, whose mass is known in terms of the international kilogram.[1] As soon as the true weight of any one piece in the set has been found, the true weights of all the others can be calculated from the relative values.[2] A weight set calibrated in this way can be used for all purposes, i.e., for the determination of absolute masses as well as for the determination of the values of ratios.

Suppose procedure 1 is adopted. The first step involves the calculation of the mass that each weight should have if one of the large weights — the 10′ g. piece, let us say — is assigned the value indicated by its denomination, i.e., 10.00000 g. These values are found by proportion. For the sake of illustration we shall consider the calibration data given in Table XL. The relative weight of the 10′ g. piece is 9.98456, the 0.01′ g. weight being assumed to weigh 0.01000 g. If the mass of this weight is now assumed to be 10.00000 g., the mass of the 5 g. piece on this basis will be $\frac{4.99223}{9.98456} \times 10.00000 = 4.99995$. Therefore, this piece is too light on the assumption that the 10′ g. piece is correct. Its correction value is $4.99995 - 5.00000 = -.00005$ or -0.05 mg. In a similar manner the corrections for all the other weights are found. To avoid the somewhat lengthy computations required in this method, it is permissible to proceed in a slightly different way. It is assumed that the 10′ g. weight actually has the mass 9.98456. Therefore it has no correction. The 5 g. piece on this basis should weigh $\frac{5}{10} \times 9.98456$ or 4.99228 g. The values in the column headed W_{10} have been obtained in a similar manner by calculating the appropriate proportional parts of the standard value 9.98456. These values are the masses that the respective pieces should have if the 10′ g. weight is assumed to weigh 9.98456 g. The difference between corresponding values of W_{10} and $W_{0.01}$ gives the correction to be applied in each case. If $W_{0.01} - W_{10}$ is positive, the weight is heavier than it should be on the assumption that the 10′ g. piece weighs 9.98456, and the correction is therefore positive. In the case of the 5 g. weight, $W_{0.01} - W_{10} = 4.99223 - 4.99228 = -0.00005$ g. or -0.05 mg. In this way the corrections recorded in the last column of the table have been obtained for all the weights. The corrections are given in milligrams.

If procedure 2 is adopted, the true weight of one of the larger pieces (10 g. or over) is determined by comparing it with a standard weight of the same denomination, the weighing being made, of course, by the method of substitution or transposition. Suppose that the true weight of the 10′ g. piece is thus found to be 10.00002 g. Evidently the correction of the 10′ g. weight is equal to + 0.02 mg. The correction for the 5 g. weight will be $4.99223 - \dfrac{(9.98456 - 0.00002)}{2} = 4.99223 - 4.99227 =$ $- 0.00004$ g. or $- 0.04$ mg.[1] In like manner the corrections are obtained for all the other weights.

---

[1] In the United States weights can be sent to the Bureau of Standards at Washington, D. C., for certification.

[2] It should be realized that if the weight compared and the standard weight are not of the same density, i.e., of different materials, then the calibrated weight will have the indicated value only when it is used in air.

TABLE XL. CALIBRATION OF WEIGHTS BY THE METHOD OF SUBSTITUTION

T	(W)	R	S	$d = \dfrac{(R_1 - R_2)}{S}$	$W_{0.01}$ (0.01′ = 0.01000 g.)	W_{10} (10′ = 10.00000 g.)	CORR.
g.	g.	div.	div./mg.	mg.	g.	g.	mg.
0.01	0.01′	+ 0.4	5.0		Standard	0.00998	+ 0.02
0.01	(Rider at 10.0)	+ 0.4		0.00	0.01000	0.00998	+ 0.02
0.01	0.01″	+ 0.4		0.00	0.01000	0.00998	+ 0.02
0.02	0.01′ 0.01″	+ 0.5					
0.02	0.02	+ 0.55		− 0.01	0.01999	0.01997	+ 0.02
0.05	0.02 0.01′ 0.01″ (Rider at 10.0)	+ 1.0					
0.05	0.05	+ 1.3		− 0.06	0.04993	0.04992	+ 0.01
0.1	0.05 etc.	+ 0.5					
0.1	0.1′	+ 1.0		− 0.10	0.09982	0.09985	− 0.03
0.1	0.1″	+ 1.0		0.00	0.09982	0.09985	− 0.03
0.2	0.1′ 0.1″	− 0.2					
0.2	0.2	0.0		− 0.04	0.19960	0.19969	− 0.09
0.5	0.2 etc.	+ 0.2					
0.5	0.5	− 0.4		+ 0.12	0.49928	0.49923	+ 0.05
1	0.5 etc.	+ 1.0					

---

[1] The strictly correct expression is

$$\left[\left(4.99223 - \frac{9.98456}{2}\right)\frac{10.00002}{9.98456}\right] + \frac{0.00002}{2} = - 0.040 \text{ mg.},$$

but this exact form need be used only when the correction runs into milligrams or the factor corresponding to 10.00002/9.98456 (the ratio of the absolute weight to the relative weight) is considerably different from unity. If the absolute (c.g.s.) corrections for the weights are desired, they may be obtained simply by adding the proper aliquots of the absolute correction to the relative corrections (the values in the last column of Table XL), the latter being multiplied if necessary by the ratio absolute weight/relative weight. These corrections are entered directly in a final column in the table. *Example.* What is the absolute correction for the 20 g. weight in Table XL? *Ans.* $\left(+ 0.03 \times \dfrac{10.00}{9.98}\right) + (2 \times 0.02) = + 0.07$ mg. Cf. E. Blade, Ind. Eng. Chem., Anal. Ed. *11*, 499 (1939).

TABLE XL. CALIBRATION OF WEIGHTS BY THE METHOD OF SUBSTITUTION — *Continued*

T	(W)	R	S	$d = \frac{(R_1 - R_2)}{S}$	$W_{0.01}$ (0.01′ = 0.01000 g.)	W_{01} (10′ = 10.00000 g.)	CORR.
g.	g.	div.	div./mg.	mg.	g.	g.	mg.
1	1′	+ 1.0	5.0	0.00	0.99844	0.99846	− 0.02
1	1″	+ 0.75		+ 0.05	0.99849	0.99846	+ 0.03
1	1‴	+ 0.65		+ 0.02	0.99851	0.99846	+ 0.05
2	1′ 1″	0.0					
2	2	+ 0.2	5.0	− 0.04	1.99689	1.99691	− 0.02
5	2 1′ 1″ 1‴	− 1.0					
5	5	− 0.5	4.9	− 0.10	4.99223	4.99228	− 0.05
10	5 2 1′ 1″ 1‴	+ 3.0					
10	10′	+ 3.0	4.8	0.00	*9.98456*	*9.98456*	0.00
10	10″	+ 3.2		− 0.04	9.98452	9.98456	− 0.04
20	10′ 10″	+ 2.4					
20	20	+ 2.1	4.4	+ 0.07	19.96915	19.96912	+ 0.03
50	20 1′ 10′ 1″ 10″ 1‴ 5 2	− 3.6					
50	50	− 1.8	3.6	− 0.50	49.92229	49.92280	− 0.51

2. *Calibration of weights using the transposition method of weighing.* This method is chiefly valuable because the precision obtainable is twice as great as in weighing by substitution.[1] An auxiliary set of weights to serve as tares is not necessary. It does not require more time to calibrate by this method than by the other, since in either method two weighings are necessary to get the difference in weight between two weights.

The method of calculating the difference in the mass of two weights which are compared is the following (Fig. 52):

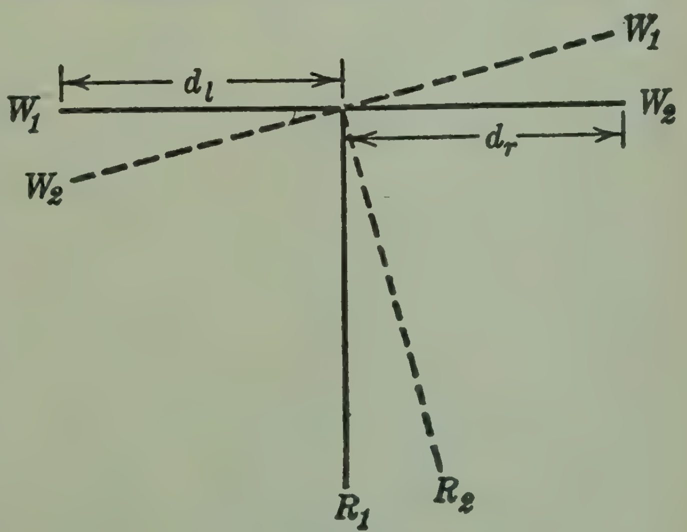


FIG. 52

---

[1] P. F. Weatherill, J. Am. Chem. Soc. *52*, 1938 (1930).

Let W_1 = weight which is *first* placed on the left pan
W_2 = weight which is *first* placed on the right pan
R_1 = rest point when W_1 is on the left pan and W_2 on the right
R_2 = rest point when W_2 is on the left pan and W_1 on the right
w = weight to be added to, or taken from, the right pan to make R_2 equal to R_1
d_l = length of left balance arm
d_r = length of right balance arm.

Then

$$W_1 d_l = W_2 d_r$$
$$W_2 d_l = (W_1 + w)d_r$$
$$(W_1 - W_2)d_l = (W_2 - W_1 - w)d_r$$

d_l may be considered equal to d_r.

Then

$$W_1 - W_2 = W_2 - W_1 - w$$
$$W_1 = W_2 - \frac{w}{2}.$$

w is calculated from R_1, R_2, and the sensitivity of the balance.

$$w = \frac{R_2 - R_1}{S}$$

where S = sensitivity.

$$\therefore W_1 = W_2 - \frac{R_2 - R_1}{2\,S}.$$

This expression gives the value of W_1 in terms of W_2. If the 0.01′ g. piece is to be compared with the 0.01″ g. and expressed in terms of the latter, then the 0.01′ g. piece is first placed on the left pan and R_1 determined. Then the weights are interchanged and R_2 found. Proceeding in this way, the value of any weight in terms of the preceding is found. To avoid confusion, the "unknown" weight is placed first on the left-hand pan.

Explanation of Table XLI. It is convenient to record the data obtained in the transposition method of weighing in a form such as that used in Table XLI, which gives the results obtained in the calibration of a set of weights used with a chainomatic balance. (W_1) indicates the denomination of the weight first placed on the left-hand pan and (W_2) that placed on the right-hand pan. The first rest point obtained in comparing two weights is given in the column headed R_1; and the second rest point, i.e.. the one obtained after the interchange of the weights, is given in column R_2. Column S gives the sensitivity at various loads. The difference in mass between the two weights compared is given in the next column. The difference is given by the expression $\frac{R_2 - R_1}{2\,S}$. W_1, the mass of (W_1) in terms of the mass of (W_2)(= W_2), is obtained from the formula $W_1 = W_2 - \frac{R_2 - R_1}{2\,S}$, the mass of the 0.1 g. piece being assumed to be 0.10000 g. The relative masses of the pieces on the basis of 10′ g. = 10.00000 g. are recorded in the column headed $W_{1\ \text{Ideal}}$. The calculations by which these values have been obtained are the same as those described in the previous section. The last column furnishes the corrections for each weight in milligrams.

TABLE XLI. CALIBRATION OF WEIGHTS BY TRANSPOSITION

(W_1)	(W_2)	R_1	R_2	S	$\frac{R_2 - R_1}{2S}$	W_2	W_1 $\left(= W_2 - \frac{R_2 - R_1}{2S}\right)$	W_1 Ideal (10′ g. = 10.00000 g.)	CORR.
g.	g.	div.	div.	div./mg.	mg.	g.	g.	g.	mg.
0.1							0.10000	0.10004	−0.04
0.1_T	0.1	+0.2	+0.4	4.0	+0.025	0.10000	0.09997		
0.2′	0.1 0.1_T	+0.75	−0.05	4.0	−0.10	0.19997	0.20007	0.20008	−0.01
0.2″	0.2′	−0.3	+0.6	4.0	+0.11	0.20007	0.19996	0.20008	−0.12
0.5	0.1 0.2′ 0.2″	+0.5	−0.3	4.0	−0.10	0.50003	0.50013	0.50020	−0.07
1′	0.1, 0.5 0.2′ 0.2″	+0.8	−0.7	4.0	−0.19	1.00016	1.00035	1.00039	−0.04
1″	1′	0.0	0.0	4.0	0.00	1.00035	1.00035	1.00039	−0.04
1‴	1′	0.0	0.0	4.0	0.00	1.00035	1.00035	1.00039	−0.04
2	1′ 1″	−0.1	0.0	4.0	+0.01	2.00070	2.00069	2.00078	−0.09
5	1′ 1″ 1‴ 2	−0.15	−0.4	4.0	−0.03	5.00174	5.00177	5.00196	−0.19
10′	1′, 1″, 1‴, 2, 5	+1.0	−2.2	3.9	−0.41	10.00351	*10.00392*	*10.00392*	0.00
10″	10′	−0.3	−1.0	3.9	−0.09	10.00392	10.00401	10.00392	+0.09
20	10′ 10″	+0.1	−2.4	3.5	−0.36	20.00793	20.00829	20.00784	+0.45
50	Σ1′—20	+0.4	−1.6	2.7	−0.37	50.10973	50.02010	50.01960	+0.50

Use of the corrections.

To find the corrected weight of an object weighed with a particular set of calibrated weights, it is only necessary to find the sum of the corrections of the pieces used and to add this sum to the nominal weight. By *sum*, the algebraic sum is of course meant. Thus, if the nominal weight of an object weighed with the set of Table XLI was found to be 7.5237 g., the corrected weight would be $7.5237 + (-0.00019 - 0.00009 - 0.00007) = 7.5233$ g. (the chain of the chainomatic balance was tested and found to be correct). In adding up the corrections, the fifth decimal is retained until the sum has been obtained, when the value is rounded off to the fourth place, i.e., to the nearest 0.1 mg. The corrected value thus obtained will be the true weight in air if the corrections used are absolute, i.e., if the true weight of any piece in the set has been determined and the corrections derived therefrom as already indicated; otherwise, the value obtained will be merely a corrected value that can be used in obtaining ratios of masses but will not represent an absolute value.[1]

Instead of adding up the respective corrections for a given combination of weights each time, it is better to construct a table that will give immediately the correction to be applied to any combination of weights. The manner of setting up and using such a table will be evident from Table XLII. The values in this table refer to the integral weights of the set of Table XLI, used with a chainomatic balance. In using a table such as this, it must be remembered that the smallest number of pieces possible is used in making a given weighing and that an unprimed weight is always used in preference to a primed, or a single-primed weight in preference to a double-primed, etc., because the table has been constructed on this basis.

TABLE XLII. CUMULATIVE WEIGHT CORRECTIONS

Integral Weights

g.	0	1	2	3	4	5	6	7	8	9
0		−0.04	−0.09	−0.13	−0.17	−0.19	−0.23	−0.28	−0.32	−0.36
10	0.00	−0.04	−0.09	−0.13	−0.17	−0.19	−0.23	−0.28	−0.32	−0.36
20	+0.45	+0.41	+0.36	+0.32	+0.28	+0.26	+0.22	+0.17	+0.13	+0.09
30	+0.45	+0.41	+0.36	+0.32	+0.28	+0.26	+0.22	+0.17	+0.13	+0.09
40	+0.54	+0.50	+0.45	+0.41	+0.37	+0.35	+0.31	+0.26	+0.22	+0.18
50	+0.50	+0.46	+0.41	+0.37	+0.33	+0.31	+0.27	+0.22	+0.18	+0.14

RULES FOR THE USE OF THE BALANCE

1. The balance should be placed in a suitable location. In the first place, it is best to keep the balance in a room separate from the laboratory proper to protect it from fumes. A room with windows facing the north and which can be kept at reasonably constant temperature makes the best balance room. The balance should not stand near a window or a radiator. It should be placed upon a solid support to protect it from vibration as much as possible. The instrument should not be exposed to direct sunlight nor to drafts.

2. The balance should be level.

3. When not in use, the beam should be raised and the pan supports should be up to prevent injury to the agate knife-edges and planes. The door of the case should be kept closed. Weights and other objects should not be left standing on the pans.

---

[1] It must be remembered that the same set of weights must then be used for all the weighings made in one analysis.

4. When an object is being weighed, the beam must first be raised and the pans arrested before any object is placed on the pans. The zero point should be determined before each weighing unless the weighing is made by difference at one sitting. In testing for equilibrium, the beam is first slowly lowered and the pans then released. Before any object or weight is taken from the pans, the latter must be arrested by bringing up the pan supports when the pointer is near the center of the scale and then raising the beam. *Fractional* weights may be *added* to the pans when the beam is released, if the pans are supported. The pans should be arrested before the rider is moved.

5. No powdered material of any kind may be placed on the pans. All substances are to be weighed in containers to prevent injury to the pans. Suitable containers for weighing are: weighing bottles, watch glasses, crucibles, and, in special cases, small Erlenmeyer flasks (50 or 100 ml.). Special care must be taken with corrosive liquids and solids that are volatile; these must be weighed in tightly closed vessels.

6. Objects to be weighed must have the temperature of the balance case; otherwise the weighing will be grossly inaccurate, and the pans may even be injured if the object is hot.

7. The balance must never be overloaded. Ascertain the maximum safe load for the balance used.

8. The balance must be kept clean. If it should happen that any substance is spilled on the pans or on the floor of the case — there is hardly any excuse for this — it must be brushed up immediately. The pans should be lightly brushed with a camel's hair brush now and then to remove dust which may have entered. Liquids must not be used for cleaning the pans.

9. Concerning weights: Weights are to be handled only with bone- or plastic-tipped forceps. In counterbalancing an object, the large weights are first tried, and then the smaller are added in systematic order. The smallest number of weights possible is always used; e.g., a 2 g. weight is used in preference to 1 + 1 g. An unprimed weight is always used in preference to a primed. The weights should be arranged systematically on the balance pan; fractional weights should not be placed upon one another. Large weights should be placed in the center of the pan to avoid troublesome oscillations that would otherwise result. Great care should be taken to avoid dropping weights. In counting the weights, the empty compartments in the box are first checked

(weights should be kept in their designated places in the box), then the weights on the pan are counted, and finally to be sure, the weights are counted as they are returned to the box. The weight box is always to be kept covered when not in use. The result of a weighing should be recorded immediately in a notebook.

10. If anything appears to be wrong with the balance or if adjustments must be made, obtain the aid of the instructor.

GENERAL REFERENCES

W. Felgentraeger, *Feine Waagen, Wägungen und Gewichte*, J. Springer, Berlin, 1932.

Article *Balance* in Thorpe's *Dictionary of Applied Chemistry*, Vol. I, p. 587, 4th ed., Longmans Green and Co., London, 1937.

PROBLEMS

1. An object on the left pan of a balance has an apparent weight of 22.4367 g. After interchanging the object and the weights, the apparent weight is 22.4377 g. (a) What is the weight of the object, and what is the ratio of the lengths of the balance arms? (b) Supposing that an error of $+0.1$ mg. is made in each weighing, what will be the error of the final result?

Ans. (a) True weight = 22.4372 g.;
ratio of arm lengths = 1.00000 : 1.00002.

2. What is the true weight of a brass weight ($d = 8.4$) having an apparent weight of 10.00000 g. in dry air at 20° and 760 mm. pressure?

Ans. 9.99857 g.

3. What weight of hydrochloric acid of density 1.1006 and containing 20.04 per cent HCl must be taken to furnish 1.000 mole of HCl if the weighing is carried out in air at 20° and 760 mm. pressure with brass weights?

4. Copper is determined in copper sulfate pentahydrate by electrolytic deposition of the metal and weighing as such. What will be the absolute error in the copper content found if the weighings are made in air under standard conditions (density of copper sulfate pentahydrate = 2.3, of copper = 8.9)?

5. The uncorrected weight of an object obtained by use of the weights of Table XL, p. 228, is 25.2003 g. What is the corrected weight?

6. If the true weight of the $10'$ g. weight of Table XLI, p. 231, is 9.99880 g., what are the absolute corrections for the 5, 2, and $1'$ g. weights?

Ans. -0.79 mg. for 5 g. weight.

7. A weight calibration gave the following relative values:

$1'$ g.	1.00248
$1''$	1.00302
$1'''$	1.00256
2	2.00391
5	5.01238
10	10.02468

If the 10 g. weight is assigned a mass of 10.00000 g., what are the respective weight corrections?

CHAPTER XIV

TECHNIQUE OF COMMON OPERATIONS OF QUANTITATIVE ANALYSIS

> *Though it may be true of some analysts that, like poets they are born, not made, yet granted intelligence, some general chemical knowledge and a fair amount of dexterity ana application, the necessary manipulative skill will come with practice, often in a surprisingly short time.* — H. S. Washington.

A gravimetric determination includes most or all of the following operations: sampling, preparation of the sample, weighing the sample, solution or fusion, evaporation, precipitation, filtration and washing, ignition or drying of the precipitate, and the weighing of the residue. A volumetric determination may include most of these operations and, in addition, the exact measurement of volume. Leaving the measurement of volume till later, we shall consider in this chapter the operations mentioned. We shall be concerned here chiefly with the mechanical side of these operations and shall touch upon their theoretical aspects only when necessary.

Quantitative analysis is an art as well as a science. Some individuals are by nature more skillful than others, but anyone can acquire sufficient skill to make an ordinary quantitative analysis satisfactorily, if he will work carefully and give some consideration to the manner in which the operations should be performed. The beginner will probably make some mistakes at first, but he should studiously avoid repeating such mistakes and should constantly strive to improve his technique.

The student should read this chapter carefully before beginning the laboratory work and should refer back to it in the course of his first analyses.

General remarks on the laboratory work.

All quantitative work demands attention to details.

The desk and the apparatus must be kept scrupulously clean and in order. All glass utensils should be rinsed with distilled water before use. They should be free from grease internally, so that water will wet the surface uniformly.[1]

---

[1] A satisfactory "cleaning solution" for most purposes is made by adding 15 g. of powdered sodium or potassium dichromate to 500 ml. of concentrated sulfuric acid. The mixture should be kept in a stoppered bottle. The vessel to be freed from grease is rinsed with the cleaning liquid, and the latter is allowed to moisten the walls for a few minutes, or longer in stubborn cases. The excess is then poured back into the stock bottle, and the vessel is rinsed successively with tap and distilled water. The corrosive nature of the cleaning fluid must not be forgotten. It should not be allowed to drip on the desk or come in contact with the skin or clothes.

Vessels should be wiped dry on the outside with a clean lintless cloth; the interiors, however, must never be touched with a cloth or anything else; in nearly all cases it makes no difference if the interior of a vessel is left moist. As soon as a piece of apparatus has been used, it should be cleaned and returned to its proper place.

During the course of the operations all vessels should be kept covered to prevent the entrance of dust, iron rust from ring stands, etc. Vessels containing solutions and solids should be numbered or labeled[1] to avoid the occurrence of mistakes or mix-ups. All observations should be recorded first-hand in a suitable notebook (*vide infra*).

The coating of ammonium salts that reagent bottles acquire on standing should be wiped off with a clean moist cloth, special attention being paid to the mouths of the bottles. It is advisable to protect the mouths of the liquid-reagent bottles by inverting small beakers over the necks if special protecting caps are not provided (p. 169).

A worker in a quantitative laboratory does not need to wear a laboratory coat or apron. "If the analyst is liable to drop acids on his clothes he is more than liable to spill some of the solutions he is analyzing" (H. S. Washington).

A few words may be said concerning precautionary measures to be taken in certain operations involving the element of danger to the worker. Operations with hydrogen sulfide, hydrogen cyanide, bromine, and other toxic gases and liquids must always be carried out in a well-ventilated hood. Likewise the volatilization of such substances as mercury and its compounds, arsenic compounds, and oxalic acid should be carried out in a hood. Hydrofluoric acid can produce very serious burns and must be handled with the greatest care; moreover hydrofluoric acid fumes are poisonous. In general all strong acids should be volatilized in a hood. Strong perchloric acid must not be heated alone with organic matter or even easily oxidized inorganic substances for fear of violent explosions;[2] particles of wax from hydrofluoric acid bottles can be dangerous. A pipet should not be used to withdraw portions of corrosive or poisonous liquids unless a trap of some kind is placed between it and the mouth.

Before beginning a determination, the student should read through the directions and make sure that he understands them. The apparatus and reagents required should be obtained if not already at hand, and a mental plan of operations made. The work should be so arranged that it can be interrupted at a suitable point. For example, a filtration should not be begun unless the washing of the precipitate can be finished immediately afterwards. Precipitations are advantageously made at the end of the laboratory period so that the precipitate can settle out, and digest if necessary, in the hours following. Lengthy evaporations should be allowed to take place overnight if possible. There should be no waste of time in an analytical laboratory. If one determination is unavoidably held up, a second should be started. For example, while crucibles are cooling in the desiccator, samples may be weighed out for another analysis; while an ignition is in progress, filtrations may be made, etc. Operations should not be hurried, for hurry may lead to loss of time through the necessity of having to repeat analyses. The aim should be to avoid repeating determinations. However, any analysis in which a known error has been made should be immediately stopped (even if the effect of the error on the result may apparently be slight), and another one begun.

---

[1] Beakers or flasks can be marked by writing with a pencil on the circular etched areas usually present. Glassware in general can be marked with a wax pencil. Porcelain crucibles can be numbered by writing with an iron-base ink on the unglazed bottoms before igniting and weighing.

[2] Perchloric acid or perchlorates must never be heated with alcoholic solutions. See E. Deisz, Z. anal. Chem. *107*, 8 (1936).

For some common operational errors, reference is made to p. 266.

Laboratory notebook.

All data should be recorded directly in a suitable laboratory notebook. The habit of making notes on loose sheets of paper must be avoided. The record of each determination should be well arranged, and no essential information should be omitted. The following items should be included: origin and or nature of sample; date or dates of the analysis; constituents determined; method of analysis (reference to source of procedure is generally sufficient); all numerical data, such as weight of sample, weight of ignited or dried precipitate in gravimetric procedures, and titration volumes, normalities, and temperature in volumetric ones; calculations; and statement of results. All heatings to constant weight must be indicated. Any observations having a bearing on the results should be recorded.

The form of record illustrated below is satisfactory for use in instructional laboratories.

Problem No. *2* Date of Report *Jan. 16, 1943*

Analysis of *Soluble Chloride*

Determination of *Chlorine*

WEIGHTS OF SAMPLES

	Det. I.	Det. II.
App. wt. of vial + subst.	*10.7481* g.	*10.5370* g.
" " " " − "	*10.5370*	*10.3378*
" " " subst.	*0.2111*	*0.1992*
Corr.	*− 0.0001*	*− 0.0002*
True wt. of subst.	*0.2110*	*0.1990*

WEIGHTS OF IGNITED RESIDUES

	(4)		(4)	
	(3)	*17.8453*	(3)	
	(2)	*17.8453*	(2)	*17.4063*
App. wt. of xble. + res.	(1)	*17.8456* g.	(1)	*17.4064* g.
" " " "		*17.4002*		*16.9862*
" " " res.		*0.4451*		*0.4201*
Corr		*0.0000*		*0.0000*
True wt. of *AgCl*		*0.4451*		*0.4201*

RESULTS: Det. I. *Cl = 52.19%* Det. II. *Cl = 52.23%*

Avg. = *52.21% Cl*

REMARKS: *Determination made according to directions on p. 000 of text. Sample air-dried. Analysis begun Jan. 15, finished Jan. 16.*

Calculations

$$\text{Chem. Factor:} \quad \frac{Cl}{AgCl} = 0.2474$$

Det. I:

$$\frac{0.2474 \times 0.4451 \times 100}{0.2110} = 52.19$$

$$\begin{array}{rcll} \log 0.2474 &=& 9.3934 - 10 & \\ 0.4451 &=& 9.6485 - 10 & \\ 100 &=& \underline{2. } & \\ && 1.0419 & \\ 0.2110 &=& \underline{9.3243 - 10} & \\ && 1.7176 \ldots\ldots\ldots\ldots\ldots\ldots & 52.19 \end{array}$$

Det. II

$$\frac{0.2474 \times 0.4201 \times 100}{0.1990} = 52.23$$

$$\begin{array}{rcll} \log 0.2474 &=& 9.3934 - 10 & \\ 0.4201 &=& 9.6234 - 10 & \\ 100 &=& \underline{2. } & \\ && 1.0168 & \\ 0.1990 &=& \underline{9.2989 - 10} & \\ && 1.7179 \ldots\ldots\ldots\ldots\ldots\ldots & 52.23 \end{array}$$

Sampling.

The axiom that no chain is stronger than its weakest link is one which applies with peculiar appropriateness to the operations of quantitative analysis. All the careful work that is put into a good analysis will go for naught if the sample taken is not representative of the mass from which it was obtained.

In obtaining a proper sample for analysis, two radically different cases are encountered:

1. The composition of a substance in the pure state is required. Here it is necessary to secure the substance in as pure a form as possible by recrystallization or other means. The specially prepared sample so obtained is then analyzed. In the analysis of a *mineral*, a similar procedure is followed, the aim here being first to separate the mineral from others which may accompany it in nature.

2. The average composition of a mass of material is required. This, the most usual case, is met with in the analysis of natural materials, such as ores, and of artificial products as well, when the aim is to determine their commercial value. Such materials are usually nonhomogeneous. An ore is a mixture of minerals, some of which are commercially valueless; the composition of an alloy may vary from point to point in the mass owing to the effects of segregation, etc. In all such cases it is essential that the small amount of material weighed out for the analysis shall have the same average composition as the large mass from which it is derived.

It is not possible in this book to describe adequately the procedure followed in the sampling of nonhomogeneous materials, and it must suffice merely to indicate how the sample is obtained and to refer the student to sources where detailed information can be secured.[1] In the case of such materials as ores and coal, a *gross sample* of several hundred, or even a thousand, pounds is obtained by combining numerous small portions taken from all parts of the mass. The number and size of the portions collected depend upon a number of factors, such as the degree of inhomogeneity, the particle size, and the size of sample finally to be submitted to the analyst. The gross sample is crushed, mixed, and subdivided; and the process is repeated as many times as necessary until a *laboratory sample* weighing from, say, twenty-five grams to a kilogram or more is obtained. The laboratory sample is kept in a well-closed container. The sample so obtained should be quite finely divided, but it may be necessary to reduce it to a still finer state of subdivision by grinding in an agate mortar as described in the next section. The sample taken for the final grinding in agate may be only a relatively small fraction of the laboratory sample, and, if so, it should be collected in small portions from different parts of the well-mixed whole (cf. the preparation of a rock sample, Chapter XLV).

---

[1] See, for example, W. W. Scott, *Standard Methods of Chemical Analysis*, Vol. II p. 1, D. Van Nostrand Co., New York, where references will be found; consult also the references in Hillebrand and Lundell, *Applied Inorganic Analysis*, p. 47.

The sampling of metals and alloys demands a different procedure because of the difficulty of pulverizing these materials. Drillings or chips representative of the cross section of the piece and free from foreign substances (oil, surface scale, etc.) are obtained by methods which will not be discussed here.[1] Important sources of error in sampling of metals are inhomogeneity, caused by segregation, and dusting, which may lead to loss of the finely divided portion of the sample having a different composition from the rest of the sample (for example, graphite in cast iron).

Grinding.

To aid the dissolution of a solid sample in a liquid, especially in a molten flux, it is often necessary to reduce the laboratory sample to a very fine state of subdivision by grinding it in an agate mortar. A *small* amount of sample, which by previous pulverization during sampling has already been powdered, is transferred to the agate mortar and ground with a circular movement of the agate pestle. The material that accumulates on the upper part of the interior of the mortar should be pushed down occasionally with the pestle, and the grinding continued until it is evident that the powder is sufficiently fine. Substances must never be *pounded* in an agate mortar, for then chips of agate may be flaked off the pestle and the mortar may even be broken on account of the comparative brittleness of agate. When the first portion of the sample has been ground sufficiently, it is transferred from the mortar to a weighing bottle or vial, if only a small amount of sample is to be ground; or else, if a considerable quantity is to be pulverized, it is carefully poured onto a square piece of glazed paper and covered with an inverted dry beaker.[2] Then another small portion of powder is placed in the mortar and ground as before. Grinding should not be continued longer than really necessary for the reasons given below. The combined ground portions should be thoroughly mixed. This is easily done when the powder has been put on glazed paper, by successively lifting the corners of the sheet and causing the powder to roll over itself many times. Care should be taken not to raise any dust.

---

[1] For a full account of the sampling of ferrous materials see Lundell, Hoffman, and Bright, *Chemical Analysis of Iron and Steel*, p. 50, John Wiley and Sons, New York, 1931.

[2] It may be advantageous to sift the powder at this point (cf. p. 735).

Finally, the powdered sample is transferred to a suitable well-stoppered vial or bottle.

Influence of grinding on the composition of the sample. By long-continued grinding, the composition of a sample may, in some cases, undergo an appreciable change:

1. If the substance ground is very hard, there may be considerable abrasion of the agate, and significant amounts of silica may be introduced into the sample.[1] Generally, however, this is not a source of serious error.

2. The water content of the sample may be altered. The finer the state of subdivision of a solid, the greater will be the amount of adsorbed (hygroscopic) moisture that it can retain (p. 133).[2] It is not possible to take account of the water thus introduced in fine grinding by drying the ground sample at 100° to 110°, because the adsorbed water may not be entirely expelled at low temperatures.

A solid containing water of crystallization may lose such water to a greater or lesser extent on grinding, as a result of the heat developed. Thus the partial dehydration of gypsum ($CaSO_4 \cdot 2\ H_2O$) on long-continued grinding is a well-known fact.[3] Furthermore, water held mechanically in the interior of crystals (vacuole water, p. 137) will be lost when the crystals are reduced to smaller dimensions, since the vacuoles are exposed and the liquid in them evaporates.

3. The chemical composition of the sample may be changed. Thus ferrous iron may be oxidized to ferric[4] with the result that erroneous results will be obtained, for instance, in the important determination of ferrous iron in rocks.[5] Calcite ($CaCO_3$) on fine grinding may lose small amounts of carbon dioxide.

It follows from all this that samples should never be ground finer than is really necessary. Just how fine a substance must be ground before analysis depends upon the sample, the method of decomposition, etc.; the analyst must use his judgment.

For the use of the "diamond" (hardened steel) mortar, see p. 735.

Drying the sample.

Often the analyst is called upon to determine the composition of a sample as he receives it. Since the water content of a sample is subject to change, due regard must be paid to this matter, for a change in the percentage of water will naturally result in a change in the percentages of the other constituents as well. It may be necessary to reserve a portion of the sample as received and determine its moisture content by drying at 105° to 110°; the determination of the other constituents may then be made on a sample suitably ground and dried at the same temperature; the percentage of the various constituents can then be reported on the original "moist basis."[6]

---

[1] W. Hempel, Z. angew. Chem. *14*, 843 (1901).

[2] See Hillebrand and Lundell, *Applied Inorganic Analysis*, p. 682, where further references will also be found.

[3] W. F. Hillebrand, J. Am. Chem. Soc. *30*, 1120 (1908).

[4] R. Mauzelius, *Sveriges geol. Undersökning*, Årsbok *1*, 1907, No. 3; W. F. Hillebrand, *The Analysis of Silicate and Carbonate Rocks*, U. S. Geol. Survey Bull. 700 (1919), pp. 60–64; Hillebrand and Lundell, *Applied Inorganic Analysis*, p. 672.

[5] Such oxidation can be prevented to some extent by grinding under alcohol (Hillebrand).

[6] For possible errors in this procedure, see p. 134.

In many cases, ground air-dried samples are weighed out for analysis and the results reported on the air-dry basis.[1] This method is satisfactory for materials which are not appreciably hygroscopic or for those in which the constituents sought are present in such small amounts that a variation in water content within reasonable limits will not sensibly affect the results. For example, metals and alloys are always weighed in the air-dry state. The chief objection to the use of air-dry samples is, of course, the possibility of a change in the water content of the substance. Variation in the moisture content of a sample may be caused by a change in the humidity of the atmosphere (cf. the notorious case of starch, p. 136), as well as by a change in the degree of subdivision of a substance at constant humidity, as already noted. Consequently, it may happen that the results of different analysts in different localities, or of the same analyst at different times, for the same sample will differ on account of a change in the moisture content. For this reason it may be necessary to dry the sample at some arbitrary temperature and report the results on the "water-free basis." It is customary to dry samples of most substances at 105° to 110°. It should be understood that a sample so dried may not be entirely free from nonessential water (p. 136), but the procedure has the advantage of furnishing a sample of fairly constant composition with respect to water. If constant weight is only slowly attained at 105° to 110°, it may be necessary to dry at some higher temperature; the temperature of drying should be reported. The possibility of change in the composition of the sample on heating must be considered (loss of water of crystallization, oxidation, etc.).

Even when the results are to be reported on the "dry basis" it may be advantageous to weigh out air-dry samples, and determine moisture in a separate portion, thus enabling the analyses to be calculated to the water-free basis. This procedure is to be recommended when the dried sample is appreciably hygroscopic; in such a case it is hardly possible to weigh out successive portions of a dried sample without having it take up moisture from the atmosphere. However, when only one or two portions are to be taken for the analysis and hygroscopic water is not to be determined, it is simpler to place the approximate weight of sample in a glass-stoppered weighing bottle and to heat to constant weight (or sometimes simply overnight) at 105° to 110° in a drying oven; after drying, the bottle is loosely stoppered, allowed to cool in a desiccator, and then weighed closed as described in the next section.

At this point it may be mentioned that obviously accidental foreign material should be removed from the sample before weighing. Included in this category are bits of cork, paper, wood, glass; oil in metal samples; pieces of steel in brass samples, etc.

Weighing the sample.

The general operation of weighing has already been described in a previous chapter.

Weighing by difference. This is the method that should usually be used in weighing samples for analysis. Briefly, the weighing is carried out as follows.

---

[1] Air-dry samples are to be used in the procedures following unless otherwise stated.

A suitable amount of sample (sufficient to give several portions) is placed in a glass-stoppered weighing bottle (Fig. 53), and the weight of the whole is obtained to the nearest tenth of a milligram on the analytical balance. The bottle is then removed from the balance with clean dry fingers[1] and unstoppered directly above the vessel into which the sample is to be poured. The stopper is held in the left hand and the bottle in the right. What is judged to be a proper weight of substance is then poured out carefully by tilting the weighing bottle slightly from the horizontal and rotating. Care should be taken to prevent raising dust. The bottle is kept over the vessel while being returned to the vertical position; it should be rotated slightly and tapped lightly when nearly vertical to cause any powder adhering to the lip to slide down into the tube; any particles on the very edge of the lip will fall into the receiving vessel. In reinserting the stopper care must be taken to avoid blowing out any particles of powder that might still be adhering to the ground-glass portion of the mouth. The bottle is then reweighed. The difference in weight gives the weight of substance taken. The weighings should be entered immediately in the *laboratory notebook.*

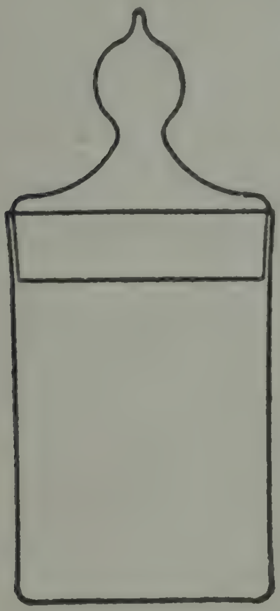


FIG. 53. Weighing bottle.

The approximate amount of substance that should be poured out to give a certain weight is soon learned by experience. A beginner should pour out a portion estimated to be safely smaller than the weight desired, then reweigh, and pour out more if necessary. If too much sample is poured out, it is not permissible to return part of it to the weighing bottle; in such an event the receiving vessel should be washed out and another attempt made. This method of weighing is not suitable for weighing out an exactly predetermined amount of sample, but this rarely needs to be done. Thus, if a procedure calls for a 0.3 g. sample, one weighing 0.25 g. to 0.35 g. will usually serve equally well; but whatever the amount, the weighing must naturally be made to 0.1 mg. If it should be necessary to take an amount of substance quite close to a specified value, successive small portions may be transferred to a weighing bottle whose weight is approximately known until the required weight is present; then the whole is weighed exactly, the contents of the weighing bottle are poured out, and the bottle with any small amount of adhering powder is weighed.[2]

---

[1] It is hardly necessary when not striving for an accuracy greater than 0.1 mg. to handle the sample bottle with a cloth or a strip of paper, provided that the fingers are clean and dry and care is taken not to heat the bottle unduly by too long or too full contact with the skin. Thus it was found that a 15 ml. weighing bottle lost in weight by 0.1 mg. after being held between the thumb and two fingers for 20 seconds (temperature of room 25°, bottle loosely stoppered). In the most careful work, however, no object to be weighed should be handled directly with the fingers; oil and moisture from the skin may increase the apparent weight, and the rise in temperature may appreciably decrease that weight. The last effect may be the more serious.

[2] It may be mentioned here that it is advantageous to have a weighing bottle tared by a similar lighter one containing enough finely divided material (such as quartz sand or metal) to counterbalance the first within a few tenths of a milligram. With such a tared weighing bottle, weighing of samples is facilitated, and wear and tear on the weights reduced.

In weighing air-dry samples, no special precautions need be taken to guard against errors due to hygroscopicity, but the case may be otherwise with substances dried at 105° or higher temperatures. It is generally not advisable to weigh out several portions of a hygroscopic substance from the same weighing bottle. Hygroscopic materials absorb moisture from the atmosphere most rapidly during the first few minutes of exposure. When dealing with such substances, it is safest to dry a single portion of sample as already described, to weigh the stoppered weighing bottle after cooling in a desiccator, to pour out the contents, and to reweigh the empty bottle.

Liquids should never be weighed in open vessels on account of evaporational losses. They may be weighed by difference if a special weighing bottle (one containing a ground-in pipet with a stopcock) is used Liquids may be conveniently weighed by the method of addition as described later, by introducing them into a weighed stoppered vessel. Great care must be taken in weighing volatile corrosive liquids to prevent the escape of fumes which might injure the balance.

Weighing by addition. Sometimes it is advantageous to weigh out a sample by addition. In this method the weight of the empty dry vessel to which the sample is to be transferred is first obtained, and the substance is then added, little by little if necessary, until the weight required is present;[1] the whole is then weighed carefully. The vessel into which the substance is weighed should be light, and should not present a large area of exposed surface in order that possible change in weight due to adsorption of moisture, electrification, heating, etc., during weighing may be kept at a minimum. It would be unthinkable to weigh a sample into a 250 ml. Erlenmeyer flask, for example, if an accuracy of 0.1 mg. were required.

This method of weighing is not suitable when the sample is to be treated directly in a beaker or flask; it may be used to weigh out a sample into a crucible prior to fusion. The method is also used when comparatively large quantities of substances must be weighed out, as in the preparation of standard solutions in volumetric analysis (p. 440). In the latter case a watch glass is employed as the weighing receptacle. It is first counterbalanced with weights or, better, with another watch glass of about the same weight; then it is removed from the pan and placed on a sheet of paper beside the balance case. The bulk of the substance is added, and the watch glass is replaced on the balance pan and tested against the weights that have been added, to see if it is heavy or light. The final adjustment in weight by adding or removing substance can be effected without removing the watch glass from the pan, if proper care is taken to avoid spilling substance in the balance. Thus, if the weight is a little too light, a spatula holding a little of the powdered substance at the end of the blade is poised over the center of the watch glass and gently tapped against a finger of the other hand to cause the powder to fall off *a little at a time*. The beam of the balance may be kept released and the pan arrests lowered all the while, if care is taken, so that the point of approximate equilibrium can be immediately noted. The excess powder on the spatula is discarded, and a small amount of the material on the watch glass is removed (after raising the beam) so as to cause the weight to become a little too light.

---

[1] A rough balance may be used first to obtain the approximate weight.

The process is repeated with the powder now on the spatula, and continuing in this manner a predetermined amount of substance is quickly weighed out, if necessary, to 0.1 mg. It hardly needs to be pointed out that substances that are hygroscopic, efflorescent, or volatile cannot be weighed accurately in this manner.

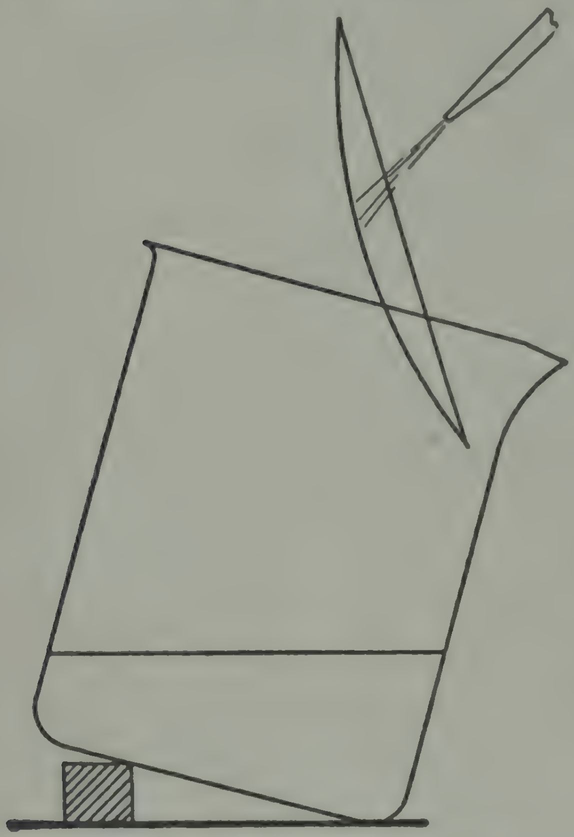


Fig. 54. Quantitative transfer of material from a watch glass to a beaker.

After the substance has been weighed out on a watch glass, it is necessary to transfer the solid without loss to some vessel in which it can be dissolved. A beaker is best used.[1] One should be chosen which has at least the same diameter as the watch glass. The latter is inclined over the beaker so that the solid slowly slides off without any dust being raised (sometimes it is advantageous to moisten the powder). The particles of material still adhering to the watch glass are washed off with a stream from the wash bottle. In this operation the beaker should be tilted so that the liquid running off the watch glass will strike the side of the beaker and flow down its side, instead of dropping directly into the solution below and splashing (Fig. 54). It is not advisable to use a brush to remove the adhering dust.

A counterbalanced weighing scoop (Fig. 55) is valuable for weighing substances into narrow-mouthed vessels.

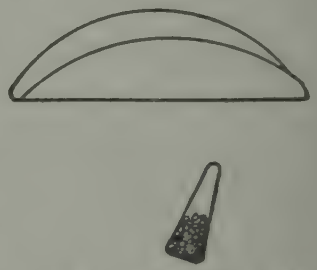


Fig. 55. Weighing scoop and counter weight.

Factor weights.

By weighing out a certain calculated amount of sample — a factor weight — the weight of ignited residue in milligrams, or the titration volume in milliliters, can be made to represent the percentage (or some simple multiple or fraction of the percentage) of the constituent desired. The analyst is thus saved the time and trouble of making the calculations; on the other hand, the time required to weigh out exactly a predetermined amount of sample may more than counterbalance the time saved in not making the calculation, and nothing is then gained. The method is not applicable if the sample changes in weight rapidly when exposed to the air, nor if it is not in a finely divided form. The device of factor weights is frequently used by analysts in the industries. Circumstances determine whether or not it is recommendable to use factor weights; it is safe to say that nothing is gained by their use when weighings must be made with an accuracy of 0.1 mg.

---

[1] If it is intended to transfer the solid to a volumetric flask, it is often advantageous to place a large dry funnel with a short wide stem in the neck of the latter to receive the material. If the solid is in the form of rather large crystals which will not pass through the stem of the funnel, or if it dissolves only slowly, the solid should be dissolved in a beaker and then transferred.

Accuracy of weighings.[1]

It is a waste of time to weigh with an accuracy much greater than that which can be attained in the subsequent steps of the analysis. This means that since we are concerned with the percentage accuracy of a result (p. 264), the actual weight of sample and the percentage of the constituent sought must both be taken into account when deciding the decimal place to which the weighing shall be made. The following expression gives the magnitude of error in absolute per cent of the constituent sought resulting from a certain error in weighing a sample of a given weight:

$$\text{Error in percentage of constituent} = \frac{\text{error in weighing sample (g.)}}{\text{weight of sample (g.)}} \times \text{percentage of constituent.}$$

For example, if a 1 g. sample of steel containing 1.0 per cent of manganese is weighed with an accuracy of 0.2 mg.,[2] the maximum error in the percentage of manganese resulting from the weighing error cannot exceed the value $\pm \frac{0.0002}{1.0} \times 1.0 = \pm\ 0.0002$ absolute per cent. Now it is impossible to carry out the other steps of the procedure in the determination of manganese with an accuracy such that the final result will differ by not more than 0.0002 per cent from the true value. Therefore weighing a 1.0 g. sample to 0.1 mg. is an unnecessary refinement. A sample of such size need not in this case be weighed closer than 0.5 mg., corresponding to a possible error of ± 1.0 mg. in weighing, which in turn corresponds to a possible maximum error of 0.001 per cent of manganese — an accuracy which it is reasonable to strive for, but one which is not easily attained.

On the other hand, in weighing out a 0.5 g. sample of iron ore containing, say, 90 per cent of Fe_2O_3, each weighing must necessarily be made to 0.1 mg. to assure a combined weighing error less than 0.1 per cent, this being the approximate error associated with the other steps of the procedure in ordinary careful analysis.

Attention is called to the fact that the size of sample that can be taken is limited by such factors as the volume of the precipitate obtained in a gravimetric procedure, or the volume of titrating solution required in a volumetric method, and the volume for proper dilution of solutions in precipitations.

Decomposition of the sample.

In most cases the method of decomposition of the sample follows from the nature of the latter and the constituent to be determined. The qualitative analysis of an entirely unknown sample will have revealed the proper procedure to follow in bringing it into solution. In any event, care must be taken to see that all components of a heterogeneous sample are completely decomposed. The reagents employed must not be such as to cause loss of the constituent sought by volatilization, or interference in the subsequent course of analysis. Thus, a steel to be analyzed for sulfur may not be dissolved in hydrochloric acid, for then hydrogen sulfide would escape; an oxidizing attack must be used.

---

[1] Cf. Chapter XV, p. 295.

[2] It is assumed, and the assumption is reasonable, that the error of a single weighing is 0.1 mg.

Specific rules for dissolving samples of different materials will not be given here. Reference to other chapters of this book will often reveal the method to follow, since a number of important classes of substances are considered.

A few words may be said concerning the common operation of dissolving a sample in water or acid. If the determination is a gravimetric one, the sample will usually be weighed into a beaker, unless certain preliminary operations, such as evaporation, must be performed prior to precipitation. The beaker should be immediately covered with a watch glass of suitable size, the convex side of the latter being turned down. The solvent is then carefully added by pouring it down the side of a glass rod having its lower end resting against the wall of the beaker to prevent splashing, the cover glass being displaced meanwhile. If the liquid added causes evolution of gas (acids with carbonates, metals, etc.), the beaker must be kept covered during the addition. It is then best to add the reagent through a small funnel with a bent stem inserted beneath the watch glass at the lip (Fig. 56), or from a pipet; the stirring rod should not be placed in the beaker until later in order that as little open space as possible may be left between the cover glass and the vessel. These precautions are necessary because when bubbles of evolved gas break at the surface of the liquid a fine spray is produced, and minute droplets would be projected out of the vessel or carried away by the escaping gas if not intercepted by the cover glass. It is almost unnecessary to say that if there is a possibility of a violent reaction when the reagent is added, water should first be added to the sample to moderate the reaction. When the gas evolution has ceased, the under side of the watch glass is rinsed off with a stream of water from the wash bottle, care being taken not to allow the water to fall directly into the solution. Solution of the sample may be hastened by stirring the liquid, or heating when necessary; boiling should be avoided except when really necessary (as in the expulsion of dissolved gases). Liquids are more safely boiled in Erlenmeyer flasks with a buret funnel in the neck to prevent mechanical loss than in covered beakers.

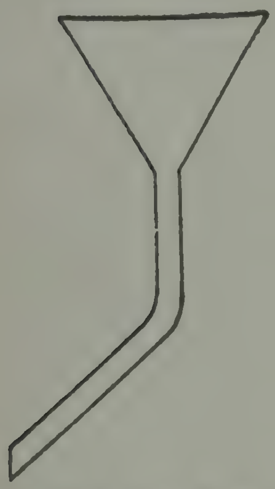


FIG. 56. Funnel with bent stem.

Fusions.

Samples which cannot be brought into solution by treatment with acids are decomposed by fusion with an appropriate reagent. Fluxes (as the reagents used in fusions are called) may be classified as acidic, basic, oxidizing, or reducing. A sample composed of a substance with acidic properties is decomposed by fusion with a basic flux, and vice versa. Thus, ferric oxide, aluminum oxide, etc., are fused with potassium pyrosulfate ($K_2SO_4 \cdot SO_3$), refractory silicates with sodium carbonate or sodium hydroxide, and so on; aluminum oxide, being amphoteric, can also be decomposed by fusion with sodium hydroxide. The very refractory mineral chromite, $FeO \cdot Cr_2O_3$, yields to the action of sodium peroxide, the chromium being oxidized to the sexivalent state.

At this point a few general statements regarding the performance of fusions may be made. Before a sample can be satisfactorily fused, it must be reduced to a very fine state of subdivision by grinding in an agate mortar, and then mixed very intimately with the flux. The mixing may usually be done in the crucible with the aid of a short stirring rod, as described on p. 406. The kind of crucible to be used in the fusion is determined by the nature of the flux. Platinum crucibles are used in sodium carbonate and potassium pyrosulfate fusions. For sodium hydroxide fusions nickel, silver, or gold crucibles are employed; and with sodium peroxide, nickel or iron crucibles are used. The crucible should never be more than half-filled with the fusion mixture and must be kept covered during the whole process. At the beginning, the heating should be very gradual to permit the quiet escape of moisture. The final temperature should not be higher than actually necessary, for otherwise there may be an undue amount of attack on the crucible by the flux in certain cases (e.g., nickel with sodium hydroxide). When the fusion has been completed, the crucible is allowed to cool somewhat; and then, while the contents are still fluid, it is grasped by the crucible tongs and tilted with a rotating motion so that the fused mass will be distributed up around the walls, thus giving a thin shell on cooling that permits easy detachment.

For detailed directions for making a sodium carbonate fusion, see p. 406, and for a pyrosulfate fusion, p. 738.

Evaporation.

In the course of an analysis it is often necessary to reduce the volume of a solution or even to carry it to dryness. Naturally vessels that are wide and shallow should be used in evaporations in order that as large a surface of liquid as possible may be exposed, and evaporation hastened. The vessels that are commonly used for the purpose are porcelain casseroles, platinum or quartz dishes, and, under certain circumstances, beakers of resistant glass. The possibility of attack of the container by the hot liquid during the prolonged contact must ever be borne in mind. It has already been pointed out (p. 174) that glass especially, even if of the resistant variety (Pyrex), is attacked by alkaline and neutral solutions and that porcelain is not exempt from action of these hot solutions. The nature of the analysis will determine whether the impurities thus introduced into the solution can give rise to errors. In work of the highest accuracy platinum dishes should usually be used for evaporations, since they are very resistant to attack by most solutions (p. 178). Porcelain vessels are to be preferred to those of resistant glass. Solutions to be evaporated in porcelain or glass should be rendered slightly acid before evaporation, if this is permissible, to lessen the attack on these vessels.

Evaporations must be conducted on a steam bath, or a low-temperature hot plate, in order that evaporation may take place without ebullition. Boiling may lead to mechanical loss even if the vessel is covered, and besides, bumping may then occur. Matters should be so arranged that large volumes of liquid can be left to evaporate on the steam bath overnight.

During evaporation, liquids must be so covered that dust and other foreign material cannot fall into the vessel, and yet the vapor be given free opportunity to escape. This may be accomplished by supporting a watch glass of Pyrex having a diameter slightly greater than the container on a glass triangle or on small V-shaped glass hooks over the top of the vessel (Fig. 57). More conveniently, a special cover glass with three molded radial ribs on the bottom that hold it away from the vessel may be used. The vessel should not be too full. If necessary the liquid can be added a little at a time to the vessel until all has been evaporated.

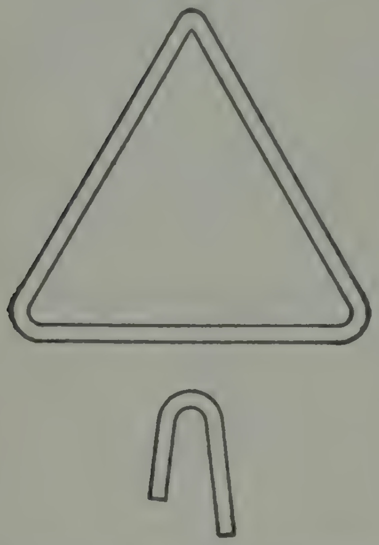


FIG. 57. Glass triangle and hook.

For evaporating small volumes of liquid rapidly, a platinum crucible placed in a "radiator" serves admirably (see the next section).

At the end of the evaporation, the sides of the vessel, the lower side of the cover glass, and the triangle or glass hooks should be rinsed off with distilled water.

Volatilization of sulfuric acid and expulsion of ammonium salts.

Sulfuric acid may be expelled by heating on a high-temperature hot plate, but the volatilization is more expeditiously accomplished in an air bath. If the solution is contained in a crucible, as is often the case, a "radiator" such as that shown in Figure 33 may be used very conveniently. The radiator consists simply of a large iron or nickel crucible fitted with a clay triangle or some other device for supporting the crucible; such a contrivance, especially made for the purpose, may also be purchased. The radiator is heated by a burner, the flame of which is adjusted so that the contents of the crucible evaporate rapidly without boiling. The liquid is heated uniformly in this arrangement, and there is no danger of loss by creeping or spattering. All evaporations of sulfuric acid, and other acids as well, should be conducted in a well-drawing hood.

Ammonium salts are expelled by cautious heating, with a free flame, of the porcelain, quartz, or platinum vessel containing the dry residue. The burner should be held in the hand and moved beneath and around the edges of the vessel. At the beginning of the heating the container should be covered with a watch glass or crucible cover, as required, to prevent loss of flying particles resulting from the expulsion of water of decrepitation; when decrepitation has ceased, any particles on the cover glass are transferred to the vessel, and further heating is continued with the latter uncovered. A crucible may conveniently be heated in a radiator. The expulsion of ammonium salts by volatilization can be accomplished quite easily when they are contained in a small platinum or porcelain vessel (crucible), but less easily when large quantities are present in a large porcelain vessel (casserole).

In the case where large amounts of ammonium chloride must be removed, destruction by oxidation with nitric acid [1] is much to be preferred to volatilization (p. 382). The solid or concentrated solution is treated with an excess of nitric acid (at least 3 g. of concentrated nitric acid for each gram of ammonium chloride) in a porcelain or glass vessel, warmed on the steam bath, and finally evaporated to dryness.

---

[1] J. Lawrence Smith, Am. J. Sci. *15*, 94 (1853).

Precipitation.

Gravimetric precipitations are made in beakers. It is often very important that the solution of the precipitant be added slowly and with efficient stirring of the solution, to avoid as much as possible local concentration of reagent, which generally leads to increased contamination of the precipitate (p. 110). For this reason it is often advisable to add the reagent solution dropwise from a pipet or buret rather than from a graduate or beaker, since the latter does not permit such uniformly gradual addition. In any case the addition must be made without splashing, i.e., the solution of the precipitant should be allowed to flow down the sides of the beaker and should not be allowed to drop in from a height. Precipitations are usually made in hot solution, since the high temperature is conducive to the formation of an easily filterable precipitate composed of large crystals; moreover, the contamination of the precipitate may be less at higher temperatures. There is no necessity, however, for heating the solution to the boiling point; it is much better to add the precipitant to a solution slightly below the boiling point to avoid the possibility of loss through the sudden liberation of steam through release of superheating. In stirring, care should be taken not to bring the stirring rod into contact with the sides or bottom of the beaker for fear of scratching the glass.

A considerable excess of precipitant is always added in a quantitative precipitation; an unnecessarily large excess is, however, to be avoided as possibly leading to increasing solubility or contamination of the precipitate. Often it is possible to calculate roughly the amount of reagent required from the weight of sample taken, assuming the latter to be composed entirely of the compound of the constituent having the lowest molecular weight. After the precipitate has settled, a few drops of reagent should always be added to see whether any more precipitate forms.

It is not advisable to filter off a precipitate immediately after it has been formed. There are several good reasons for not so doing. In the first place, solubility equilibrium may not be reached at once, especially with substances tending to form supersaturated solutions. Then, the precipitate may sometimes be obtained in a coarser, more easily filterable form, by letting it stand in contact with the hot mother liquor for some time (p. 122). Moreover, it is found in many cases that the amount of coprecipitated substance in the precipitate decreases on standing, this effect being a consequence of the growth and perfection of the crystalline particles of the precipitate. For these reasons it is frequently recommendable to *digest* a precipitate before filtration by letting it stand on the steam bath for some hours or overnight. Sometimes, however, so little is gained by this procedure that it is as well to filter off the precipitate an hour or so after precipitation; indeed, it is sometimes positively disadvantageous to let a precipitate stand for any length of time (precipitation of ferric hydroxide and other hydroxides or hydrous oxides with ammonia, especially in the presence of calcium; precipitation of calcium with oxalate in the presence of magnesium, etc.). Circumstances decide the procedure to be followed.

If the solubility of the precipitate is large, it may be necessary to let the solution come to room temperature before filtration. The liquid should then be stirred occasionally during the cooling.

Precipitation with hydrogen sulfide. It is best, in most cases, to make precipitations with hydrogen sulfide by leading the washed gas through a one-hole rubber stopper into an Erlenmeyer flask in which the solution is contained. The entrance tube should not dip into the liquid but should be close to the surface (Fig. 58). After the air has been displaced from the flask, the stopper can be pressed into place and the absorption of hydrogen sulfide allowed to take place under the slight pressure of the gas, aided by swirling of the liquid.

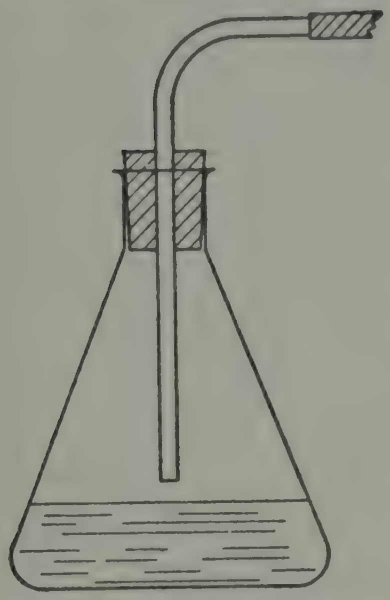


FIG. 58. Precipitation with hydrogen sulfide.

Filtration and washing of precipitates.

Filtration through paper. Filter paper is especially suitable for the collection of precipitates that are gelatinous[1] and for those that must be heated to a very high temperature before weighing.

Owing to the hygroscopic nature of paper, precipitates cannot be weighed in a paper filter after washing and drying; it is necessary to ignite the filter and its contents in a crucible and weigh the residue, which corresponds to the precipitate and a negligible amount of ash. If in burning off the paper the precipitate tends to be reduced by the carbon or the gases formed, or otherwise affected, it is necessary to separate the bulk of the precipitate from the paper and ignite the latter, then to convert the small amount of adhering precipitate, which may have been reduced, to the original form by the use of proper reagents, and finally to add the main portion of the precipitate which has been reserved in the meantime. Such a procedure is so troublesome and conducive to error that it may be stated as a general rule that if a precipitate will be changed chemically by the action of the paper during the ignition it should not be filtered off on paper. The silver halides, for example, should not be caught on paper because they are easily reduced to free silver on ignition. On the other hand, barium sulfate may be collected in paper, for although it may suffer a slight reduction to sulfide on ignition, it is easily oxidized back to sulfate on continued heating with free access of air.

Before beginning a filtration through paper, it should be decided what size and what fineness of *quantitative* filter paper is best suited for the particular filtration. In the first place, the size of the paper chosen should not be larger than is really necessary, and it should be remembered that the size is determined by the amount of precipitate to be collected rather than by the volume of liquid to be filtered. The precipitate should preferably fill not more than a third of the filter and never more than one half. Circles 9 cm. in diameter find most frequent use. When the precipitate is to be weighed, quantitative ("ashless") paper (p. 184) must always be used. If the ash amounts to more than 0.1 mg., its weight should be deducted from the weight of the ignited residue.[2]

The method of preparing a filter for use is as follows. First, the dry paper is folded exactly in half and then once again through the center so that the two halves of the first crease do not quite coincide. When a paper so folded is opened, the apical angle of the cone will be slightly greater than 60°. Such a filter when placed in a 60° funnel will not quite fit the walls of the latter at the apex, but will do so at the top. A paper folded in this manner will filter more rapidly than one which adheres to the funnel over its whole area, for the liquid which has penetrated the former filter will run down unimpeded through the narrow space between paper and glass, and at the same time the top of the paper will fit the funnel so well that no air is likely to be drawn in between the two. The exact angle at which the second fold should be made depends upon the apical angle of the funnel used — which is rarely exactly 60°. It may be necessary to refold the paper once or twice to get it to fit properly. The crease at the apex of the filter should not be flattened too much for fear of weakening the tip. The corner of the fold on the outside should be torn off (Fig. 59) in order that the paper may be fitted snugly to the funnel when it is later moistened.

---

[1] The use of filter-paper pulp to aid the filtration of gelatinous precipitates has already been referred to, p. 185.

[2] The weight of ash of a single filter can be determined by igniting a number of papers together.

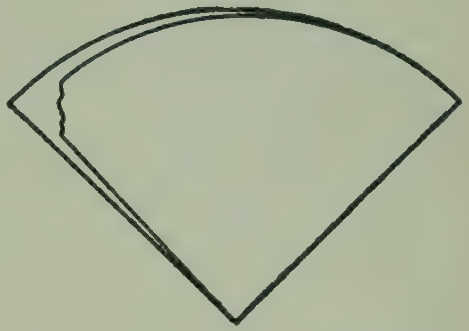


Fig. 59. Correct method of folding a filter paper.

The filter paper is now placed in a funnel of proper size; the top of the filter should fall $\frac{1}{2}$ to 1 cm. below the rim of the funnel. The paper is moistened with water from the wash bottle, and its upper third gently pressed against the glass with the finger. When water is now poured into the filter, the stem of the funnel should fill. If it does not do so (as is likely to happen if the stem is too wide or the glass is greasy), the end of the funnel stem should be closed with the finger and the stem allowed to fill until the water rises into the apex and above. The air entrapped between the glass and paper is permitted to escape by pulling the paper gently aside at one point. The paper is then carefully refitted to the glass all around, and the finger removed; the stem should remain filled with liquid. The glass above the paper should not be moistened in these preliminaries. It is very important to have an unbroken column of liquid in the stem, because the weight of such a column produces a gentle suction that greatly hastens filtration.

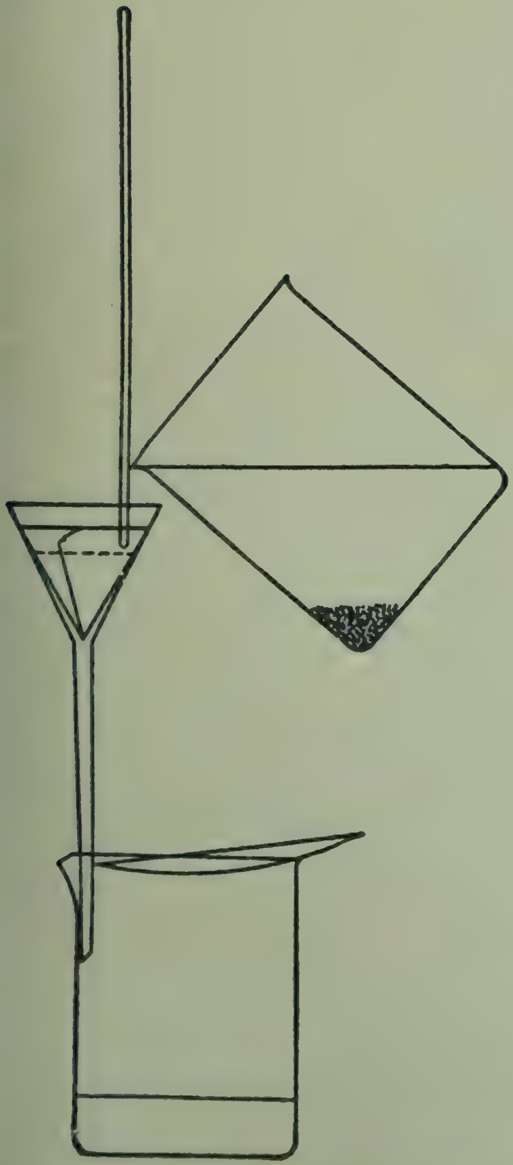


Fig. 60. Filtration through paper.

When the filter paper has been properly fitted to the funnel, the latter is placed in a funnel stand, and a clean beaker is put into position beneath. The funnel stem should touch the side of the beaker to prevent splashing and should be well above the bottom of the vessel (Fig. 60); the stem of the funnel must never extend into the liquid in the receiving vessel. Everything is now in readiness for filtration. The beaker containing the liquid to be filtered is taken in the right hand and held slightly above and to the right of the funnel. The stirring rod is removed from the beaker, care being taken that no drops of liquid are lost, and held vertically over the funnel. The lower end of the stirring rod should be very close to, but should not touch, the filter paper on the side having three thicknesses of paper. The lip of the beaker is placed against the rod, and the vessel is slowly inclined until the liquid flows down the rod into the paper without splashing. It is absolutely inadmissible to transfer liquids in quantitative operations without the use of a stirring rod. The filter should never be filled to the brim — the level of the liquid should not rise closer than to within 2 or 3 mm. of the top of the paper. In transferring the liquid to the filter care should be taken not to disturb the precipitate in the bottom of the vessel. Even if the supernatant liquid appears to be entirely clear, it must nevertheless always be passed through the filter.

As long as the liquid flows through the filter freely, the beaker is kept inclined, and a slow stream is poured into the funnel. When most of the supernatant liquid has been poured off, particles of precipitate will come over, and the speed of filtration will gradually decrease owing to the filling of the pores of the paper with precipitate. When this occurs, the stirring rod is returned to the beaker, and the latter is set down while one waits for the filter to empty. It is advisable to keep the filter always fairly full of liquid to prevent the stem from emptying. The precipitate in the bottom of the beaker should be disturbed as little as possible. It is important that the stirring rod be kept out of the lip of the beaker, which will contain adhering precipitate. At this point the filtrate should be carefully examined for particles of precipitate that may have run through the paper. If such are found, the liquid in the receiving beaker must be passed through the filter, and the new filtrate caught in a fresh beaker. If the precipitate persists in running through, the filter paper used is too coarse, or else the precipitate is too fine for a quantitative filtration.

When as much as possible of the supernatant liquid has been poured through and a relatively small volume of liquid with precipitate is left, washing by *decantation* is begun. A stream of wash liquid from the wash bottle is directed against the sides of the beaker to wash down adhering particles, the precipitate is stirred up and then allowed to settle. The amount of wash liquid to be added cannot be specified. It depends upon the amount of precipitate, its character, etc.; the analyst must use his own judgment. When the supernatant liquid is clear, it is poured into the filter, as much as possible of the precipitate being kept in the beaker. Another portion of wash liquid is added to the beaker, and the process is repeated. The filter is allowed to drain completely after each addition. The operation is repeated three or four times or as many times as is deemed expedient.

It is not always advantageous to wash by decantation. If the precipitate is coarse-grained and filters well, not much is gained by applying the decantation method of washing. In such a case it is better to transfer the precipitate to the paper immediately after the supernatant precipitation liquid has been passed through the filter. Gelatinous precipitates which tend to clog the paper and make filtration slow can sometimes be washed free of most of the soluble salts by decantation, and the final washing made upon the paper. But even with such precipitates, not much is gained by washing by decantation if the precipitate is very voluminous and settles only slowly. Washing by decantation is objectionable if the volume of the filtrate must be kept as small as possible. The method may well be applied when the precipitate is to be dissolved and reprecipitated. In this case all soluble salts need not be removed; it is only necessary to make their concentration very small to prevent appreciable coprecipitation (p. 119), and this can be done by washing a number of times by decantation. To dissolve the precipitate for further treatment, the beaker containing the bulk of the precipitate is put in the place of the one containing the filtrate, and the relatively small amount of precipitate on the filter is dissolved by filling the latter with the proper solvent and adding more as required. When all the precipitate has been dissolved, the paper is washed and the washings collected in the same beaker. All the precipitate in the latter is dissolved by stirring and bringing the solution into contact with all parts of the vessel and rod. The substance, now entirely in solution, is reprecipitated by adding the proper reagent and a little of the original precipitant to diminish the solubility. After standing, the precipitate is filtered off (possibly on the same filter if this has been washed with water to remove the solvent) and carefully washed as described below. The filtrate from the second precipitation is combined with that from the first, and the combined solutions are reserved if necessary.

Whether or not washing by decantation has been resorted to, the main bulk of the precipitate is transferred to the filter by mixing with wash solution and pouring off the suspension, the process being repeated until most of the solid is on the paper. The precipitate adhering to the sides and bottom of the precipitation beaker is removed in the following manner. The beaker is taken in the left hand, and the stirring rod is put across its top and held in place with the left index finger. The rod is made to rest against the lip of the beaker and should project 2 or 3 cm. beyond. The beaker is then inclined over the funnel so that liquid can run out of it, down the rod into the paper without spattering. The wash bottle is grasped in the right hand, and a stream of wash solution is directed against the inside of the beaker so that the particles of precipitate are washed out into the filter (Fig. 61). After this treatment there will usually still be small amounts of precipitate adhering to the walls. These are removed by moistening the walls and rubbing gently with a "policeman" (Fig. 62). The whole interior of the beaker, as well as the surface of the stirring rod, is thus gone over. When all particles have been dislodged, the policeman is rinsed off and removed from the

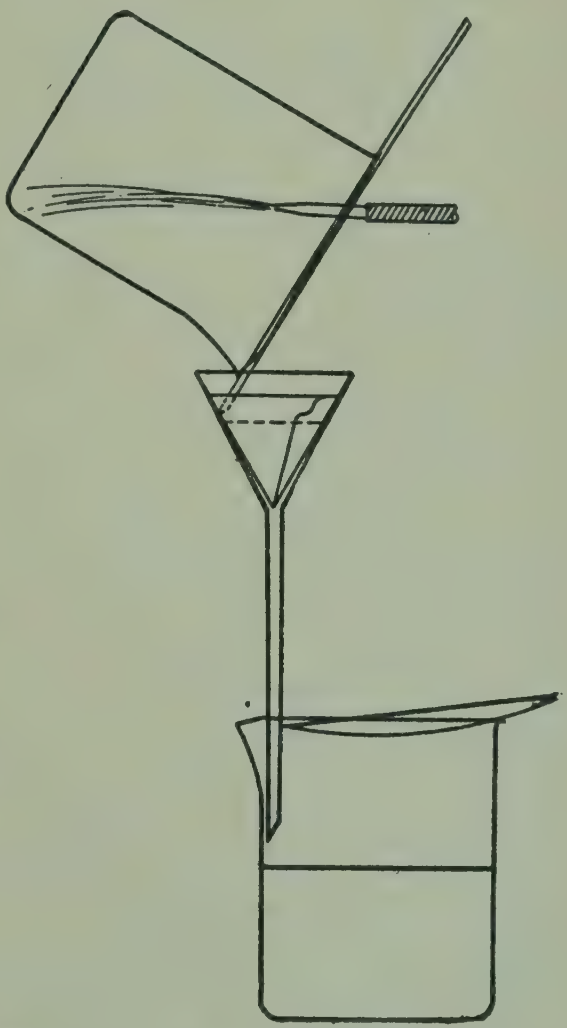


FIG. 61. Transfer of precipitate from beaker to filter paper.

beaker.[1] The small amount of precipitate thus loosened is washed into the filter in the same manner as before. The beaker and stirring rod should finally be held up to the light and carefully examined for specks of precipitate or unrubbed surface, and the treatment repeated if necessary.

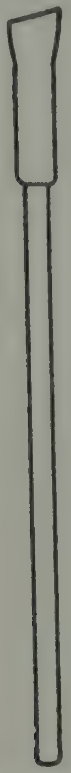


FIG. 62. Stirring rod with policeman.

As soon as the precipitate has all been transferred to the filter, washing should be begun. A precipitate should not be allowed to stand on the filter for any length of time unwashed. The mass will crack and cake together, and it will be virtually impossible to wash it free of soluble salts when it is in this condition. The kind of wash solution to be used depends upon the precipitate (and to a lesser extent upon the substances in solution). Two factors especially must be considered: the solubility of the precipitate and its peptizability. If a precipitate is appreciably soluble in water, it cannot, of course, be washed with this liquid. This difficulty can be overcome, when a cation is being determined, by washing the precipitate with a dilute solution of an ammonium salt having an ion in common with the precipitate. The ammonium salt remaining with the precipitate after the washing is volatilized on ignition at a low temperature.[2] Thus in the gravimetric determination of calcium as oxalate, the precipitate is washed with dilute ammonium oxalate. Even if the precipitate is so slightly soluble in water that no error is to be feared from solubility loss, it is sometimes not advisable to wash with pure water, for peptization (p. 97) may then occur and the washings will run through the filter turbid.[3] This phenomenon can occur with coagulated colloidal precipitates but usually not with microcrystalline precipitates. To prevent peptization, a solution of some electrolyte is used for washing. The electrolyte should be one that can be removed easily (volatilized) in the preparation of the precipitate for weighing. For this reason dilute acids, ammonia, or ammonium salts are used. The silver halides, for example, are washed with very dilute nitric acid, in which they are not appreciably soluble. In some cases, washing with a solution of a salt having an ion in common with the precipitate is out of the question, as, for example, when calcium oxalate is to be titrated with permanganate after precipitation (p. 605). In such a case water is of necessity used for washing, and care is taken to limit the amount to that actually necessary.[4] Whether a wash liquid should be used cold or hot depends on the solubility of the precipitate at higher temperatures. When permissible, hot wash liquids are employed because the solubility of foreign salts is usually greater in hot solution, and the speed of filtration is then greater owing to the decrease in viscosity of liquids with an increase in temperature.

---

[1] The policeman should not be allowed to stand in a solution for any length of time; it is not a substitute for a stirring rod and should not be used in transferring liquids.

[2] If the precipitate is to be dried at a low temperature, e.g., 110°, the nonvolatile constituents of the wash solution can often be removed by finally washing with a water-alcohol solution, in which most inorganic precipitates are virtually insoluble.

[3] Moreover, hydrolysis of certain substances in solution may occur, leading to contamination of the precipitate. Thus ferric salts are hydrolyzed to basic salts by water. Using dilute hydrochloric acid as wash liquid prevents this (cf. p. 40).

[4] Sometimes it is possible to use a saturated solution of the slightly soluble substance in water for washing. Mixtures of alcohol and water can be used in certain cases.

Hydrolyzable precipitates require the use of a wash liquid containing a substance repressing the hydrolysis (p. 40).

It may be added here that the wash solution running through the filter is never saturated with respect to the precipitate so that solubility losses are often much less than would be expected from solubility data.

It is easy to show that washing is done more efficiently with many small portions of liquid than with few large portions, the total volume being the same in both cases. In other words, a smaller volume of liquid will suffice if small portions are added at a time.

Let v = volume (ml.) of liquid remaining with the precipitate after draining
V = volume of wash liquid added each time
C_0 = concentration (g./ml.) of soluble substances in original solution; C_1 = the same concentration in the adhering solution after the first washing, C_2 = the concentration after the second washing, etc.

After the precipitate has been washed once and allowed to drain, the concentration of foreign substances in the adhering solution is evidently given by the following expression, if complete mixing is assumed:

$$C_1 = \frac{v}{V + v} C_0.$$

After the second washing the concentration is:

$$C_2 = \frac{v}{V + v} C_1 = \left(\frac{v}{V + v}\right)^2 C_0,$$

and after n washings, $C_n = \left(\frac{v}{V + v}\right)^n C_0.$

The weight of foreign substance, W_n, in grams remaining in the solution adhering to the precipitate after the nth washing will be:

$$W_n = vC_n = \left(\frac{v}{V + v}\right)^n vC_0.$$

It will be apparent from this expression that with a given volume of wash liquid the precipitate can be more completely washed if many small portions are used than if a few large portions are employed. By way of illustration, suppose that a precipitate is washed in one case with five portions of water of 10 ml. each, and in the other with two portions of 25 ml. Assume that $v = 1$ and $C_0 = 1$. In the first case, after washing five times, the amount of foreign substance remaining with the precipitate will be:

$$W_5 = \left(\frac{1}{1 + 10}\right)^5 \times 1 \times 1 = 7 \times 10^{-6}\text{ g.}$$

whereas in the second case, after two washings with the same total volume of liquid:

$$W_2 = \left(\frac{1}{1 + 25}\right)^2 \times 1 \times 1 = 1.5 \times 10^{-3}\text{ g.}$$

Now, it must be emphasized that foreign substances are not so easily removed from the precipitate by washing as the above formulas would indicate. The preceding expressions have been derived on the assumption that the solution of the foreign substances is simply mechanically associated with the particles of the precipitate. This is far from being true. Actually part of the foreign substances are more or less tenaciously retained at the surface of the particles as the result of *adsorption* (p. 115). Consequently the concentration of the foreign substances in the solution adhering to the precipitate decreases much more slowly on successive washings than is indicated above, and a greater number of portions of wash liquid must be used to reduce the contaminating substances to a permissible small amount than would be expected from the mechanical theory of washing.[1] Some of the solution is, moreover, more or less isolated in the interior of the mass of the precipitate, being held by capillarity between the grains, and is only slowly removed by the percolating wash liquid. However, it is still true that the washing will be more efficient, the smaller the portions used.

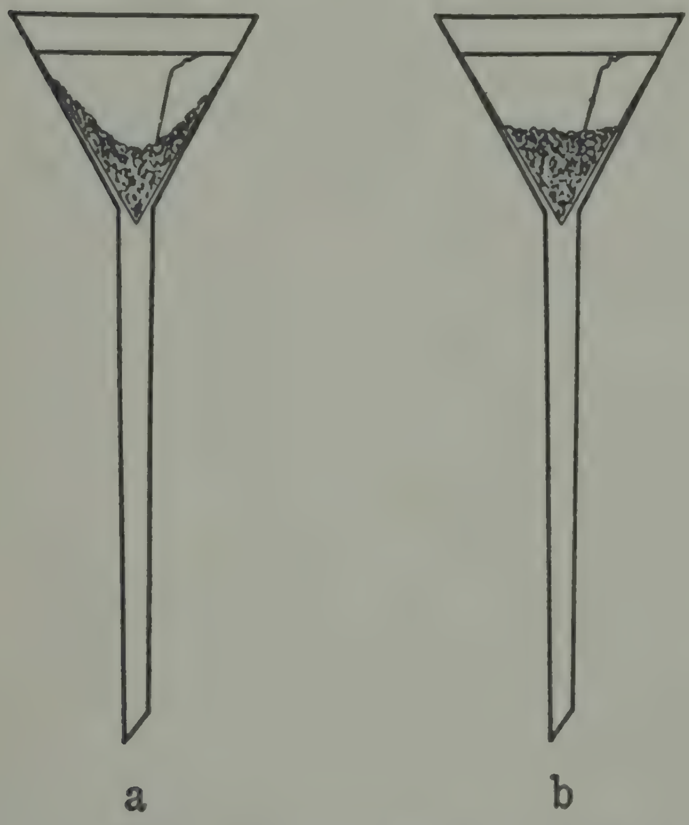


Fig. 63. Illustrating the washing of precipitates in paper. a, before washing; b, after washing.

Special attention is called to the fact that washing does not remove to any appreciable extent contaminants occluded in the interior of the particles of the precipitate.

To return to the consideration of the technique of washing. Before beginning the washing on the paper, it is advisable to substitute a clean empty beaker for the one containing the filtrate, so that in case the precipitate should run through at the start of the washing it will not be necessary to refilter a large volume of solution. The stream from the wash bottle is now directed around the top of the filter paper — which part will be free from precipitate if the previous directions have been followed—to remove soluble substances. It is important not to neglect this part of the filter. After it has been carefully washed all the way around with three or four small portions of solution, the thin layer of precipitate on the upper part of the paper is attended to. This precipitate is washed down into the filter with a gentle stream of liquid from the wash bottle. The jet of liquid must not be allowed to strike the precipitate suddenly, for then, more likely than not, some of the latter will be thrown out of the filter. When the filter is about one-half full of liquid, the stream is stopped, and the paper is allowed to drain completely. The washing-down of the precipitate is continued until it has been collected in the apex of the filter (Fig. 63). When this has been accomplished, the jet from the wash bottle is again directed at the upper portions of the paper, beginning very near the top edge, and continued downward. Each time the filter is filled approximately half-full — if the precipitate is compact and small in amount, less liquid need be used, whereas if it is very voluminous (hydrous oxides), a larger volume is required; in any event the collected precipitate should be covered with liquid each time. It is impossible to give exact directions; the student will soon acquire good judgment in these matters if he considers the operations critically.

---

[1] For an expression taking adsorbability into account, see Wilhelm Ostwald, *The Scientific Foundations of Analytical Chemistry*, translated by G. M'Gowan p. 20, Macmillan and Co., London, 1908.

After, say, eight or ten drainings, completeness of washing should be tested by adding to the last washings a reagent which will give a precipitate or coloration with a substance in the solution in which the precipitate was formed. For example, the presence of chloride in the washings, as revealed by the formation of a precipitate or opalescence when silver nitrate is added, may frequently be made the criterion of complete washing, since chloride ion is so often present in solutions. In testing for complete washing, the stem of the funnel is washed off with a few drops of water to remove any of the earlier solution possibly adhering on the outside tip (the stem should never be allowed to dip into the liquid in the receiving vessel), and a milliliter or so of the last washings is collected in a rinsed test tube. A drop of the appropriate reagent is added, and the solution is examined for turbidity (Fig. 64). If a precipitate is formed, the washing is repeated two or three times and the test again made; the process is repeated until the washings give no reaction, or at most only an exceedingly faint one. It is evident that the washings should not be tested too early in the process, if the filtrate is to be analyzed for another constituent. The ignition of the precipitate is described on p. 259.

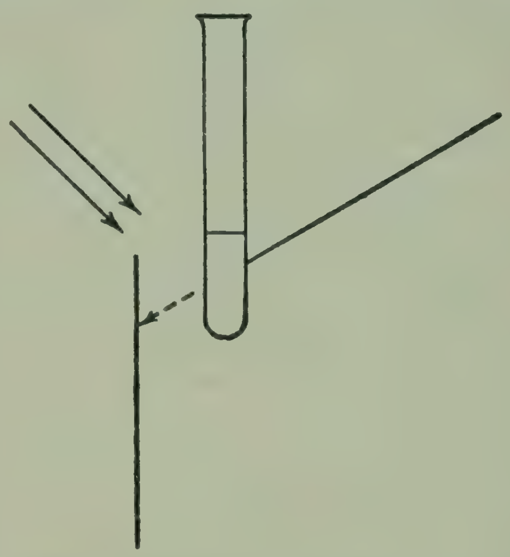


FIG. 64. Examination of a solution for turbidity against a dark background.

In certain cases it is necessary to filter a solution containing a precipitate without altering the concentration of the dissolved substance. For example, it may be desired to take aliquot parts of an ore sample by diluting a solution of the same containing undissolved gangue material to the mark in a volumetric flask and then measuring out definite amounts of the clear solution. In such cases the filtration can be made through a dry filter paper placed in a dry funnel, the filtrate being received in a dry vessel. The first portions of liquid running through the paper should be discarded, because they may contain less of the dissolved substance than the original solution because of adsorption of solute by the filter paper. Naturally care must be taken to prevent evaporation of solvent by keeping the vessels covered.

Filtration with filter crucibles.[1] The use of filter crucibles has the following advantages over the use of paper in filtration:

---

[1] See p. 185 for a description of filter crucibles and preparation of the Gooch crucible.

1. Owing to the use of suction, filtration and washing require less time.
2. Washing is much easier and more perfect.
3. There is no danger of change in the composition of the precipitate by the action of reducing gases and carbon as in the case of paper, or of decomposition or volatilization at the temperature required to burn away the carbon.
4. Drying or heating of the precipitate requires no special attention and is rapid.

In certain cases filter crucibles are not suitable:

1. Gelatinous precipitates cannot be filtered.
2. Precipitates that cannot easily be dissolved out of the crucible sometimes cannot be filtered advantageously.
3. The crucible may not resist the temperature required for the ignition (sintered-glass crucibles).
4. If the ignited residue requires treatment with a liquid reagent, a filter crucible may not be suitable.

Unless there is a special objection to its use, a filter crucible should be used in preference to filter paper.

On account of the labor involved in their preparation and the somewhat unstable character of their asbestos mats, Gooch crucibles are less preferable than the other kinds of filter crucibles. They are, however, cheap, can be heated to a high temperature, and are often very satisfactory. The choice between sintered-glass and porous porcelain filter crucibles is determined mainly by the temperature to which the precipitate in question is to be heated. The former can be heated to a maximum temperature of 500°, but only if the heating and cooling be very gradual. Porcelain filter crucibles can be heated to 1000° with safety.

Whatever the crucible used, it must first be washed with water or dilute acid to remove soluble substances and then dried to constant weight at the same temperature to which the precipitate is later to be heated. It is then set in a Gooch funnel (p. 186), care being taken that the bottom of the crucible extends well into the latter so that there will be no chance of the filtrate coming into contact with the rubber. After gentle suction has been applied, the supernatant liquid in the precipitation vessel is carefully poured into the crucible with the aid of a stirring rod touching the side of the latter. The precipitate is transferred to the crucible in the manner already described. In washing the precipitate, the stream from the wash bottle is first directed to the top of the crucible; the jet should not strike the precipitate in the bottom. The suction should not be so strong that the wash solution is immediately drawn through the crucible; it is essential that the wash liquid remain in contact with the precipitate for some moments. In testing for completeness of washing, a small test tube suspended within the suction flask by means of a cord may be used to collect small portions of the liquid. If the filtrate is to be used, care should be taken to see that no solution is carried off into the vacuum line; there is not much danger of this occurring if the stem of the funnel projects well into the flask and too strong suction is not used.

Drying and ignition of precipitates.

Ignition of precipitates in paper. The filter paper and its contents may first be dried, if desired, by covering the funnel with a circle of ordinary filter paper folded down around the rim of the latter, placing the whole in a drying oven, and heating at 100°. This preliminary drying is by no means necessary, although sometimes advantageous in the case of bulky gelatinous precipitates that hold much water. Usually the well-drained filter may be placed directly in the weighed crucible and dried therein before ignition; indeed, this is often to be preferred, because folding up a dry filter may lead to a slight loss of the contents.

The filter is carefully loosened from the funnel, lifted out, and the edges of the paper folded down and over the precipitate so as to enclose it completely. The package is placed in a previously weighed crucible with the side having the three thicknesses of paper uppermost; if necessary the whole is gently pressed down into the bottom of the crucible without breaking the paper. The crucible is set vertically in a triangle on a ring stand[1] and heated over a small Tirrill flame. A flame about 2 cm. high is suitable when the crucible is placed about 10 cm. above the tip. The crucible should be covered, but the cover is displaced a little to one side so that the steam can easily escape. During the heating the water must not boil or spatter. The heating must be slow, or else the precipitate may be projected against the cover or even out of the crucible. When all the moisture has been expelled and there are no drops of water on the under side of the cover, the crucible is gradually lowered and the height of the flame increased if necessary, to slowly carbonize the paper. The crucible is kept covered during the carbonization, but the cover is lifted now and then to enable the progress of the charring to be followed. The paper must never burst into flame, nor should the escaping gases ignite. When the paper is completely charred, as revealed by its black color, and no more gases escape, the crucible is inclined on the triangle at an angle of about 45°, and the cover is placed on one side so that air can enter. It may even be advantageous on

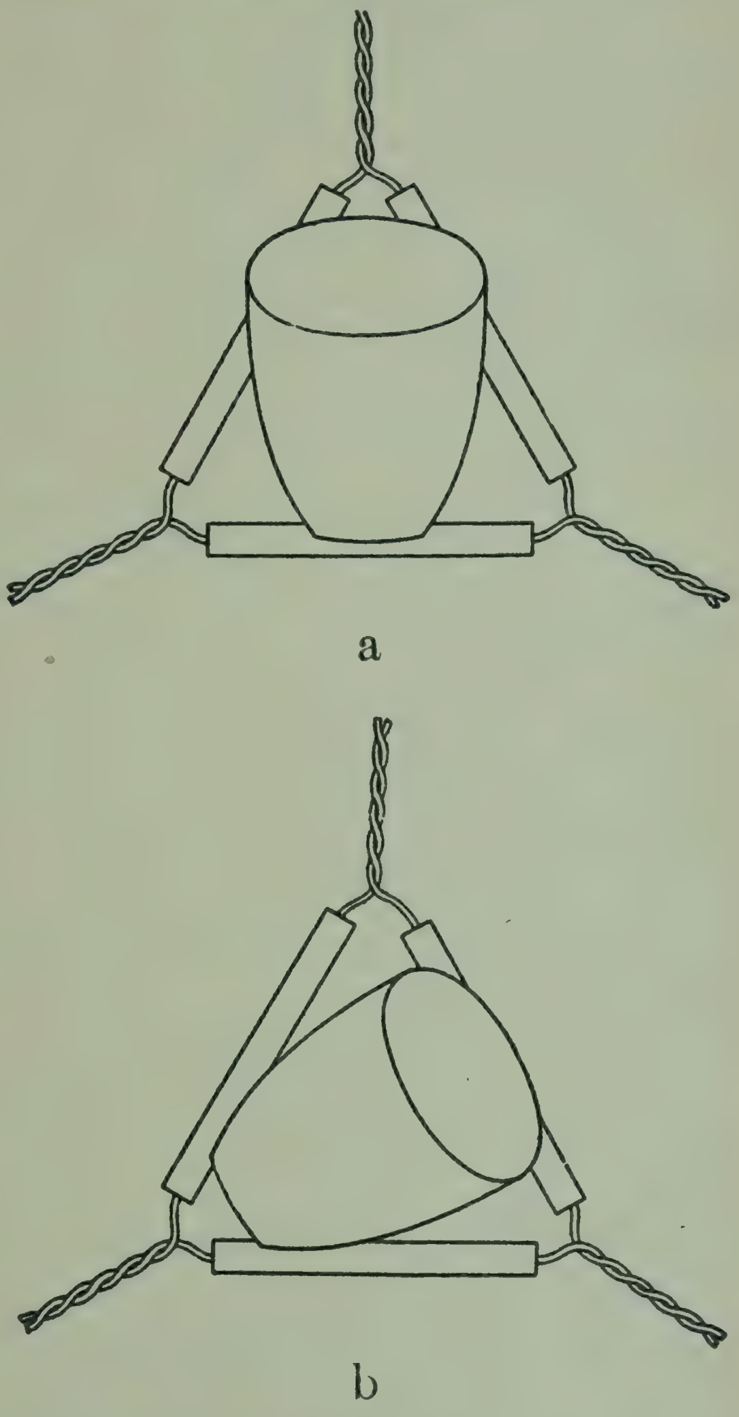


Fig. 65. Correct (a) and incorrect (b) position of inclined crucible on triangle.

---

[1] The triangle supporting the crucible should be placed on the ring of a ring stand and not on a tripod in order that the crucible may be raised or lowered as may be necessary during the course of the drying and ignition.

occasion to incline the crucible even more and lean the cover steeply against the mouth as shown in Figure 66. The crucible is heated to low redness at the bottom. The flame must not be allowed to approach the mouth of the crucible, for then currents of air set up might sweep out particles of light precipitate, and besides, the reducing gases finding admittance might reduce the precipitate and even injure the crucible if this be of platinum. A flame larger than really necessary should be avoided.

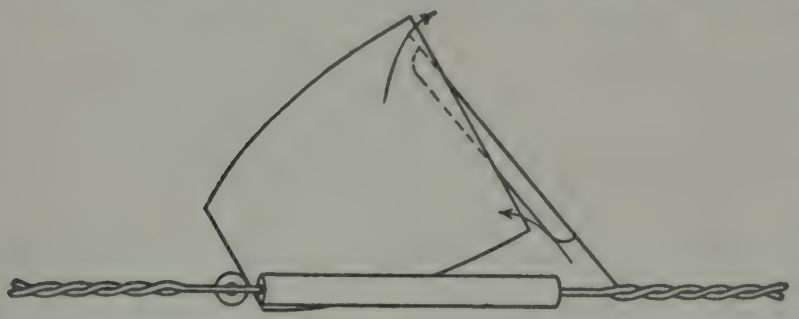


FIG. 66. Position of crucible and cover in burning off carbon of filter paper (a platinum crucible is represented).

After the carbon has all been burned away, the crucible is placed in the upright position and covered (any carbon on the cover may be burned away by holding the latter with the crucible tongs over the flame). The flame is adjusted to give the temperature desired, and the ignition is continued for 15 to 30 minutes in the usual case, or longer if required. The crucible must not be enveloped by the flame and must be kept out of the inner cone of the latter. If the temperature of ignition must be regulated over a narrow range to prevent decomposition or volatilization of the weighing form, an electric muffle furnace with a pyrometer is used in place of a burner. Such a source of heat is, moreover, to be preferred when a reducing atmosphere or contamination by gases of the flame (sulfur oxides) is to be avoided, or when porcelain crucibles must be heated to high temperatures (cf. p. 177).

If, in gas heating, a Tirrill burner will not supply a sufficiently high temperature, a Meker burner or a blast lamp is used. In using the latter, the covered crucible should be set vertically in the triangle and the flame of the blast directed obliquely against the bottom and the lower part of the crucible; the flame must not strike the upper part of the crucible.

When the ignition is ended, the crucible is allowed to cool below redness in the air, and then while still hot it is placed covered in the desiccator.[1] After the crucible has come to room temperature (p. 223), it is weighed, and ignited again for 10 to 15 minutes. The heating, cooling, and weighing are repeated until constant weight [2] is attained. In transferring the cooled crucible from the desiccator to the balance, the crucible tongs should always be used.

As regards the choice of crucibles for ignitions, it may be said that platinum crucibles are to be preferred to those of porcelain, because the former heat and cool more quickly than the latter and can be raised to a higher temperature in the flame. In some ignitions platinum must be used, as for example in the ignition of silica when treatment with hydrofluoric acid is to follow. Owing to the high cost of platinum, porcelain crucibles must often be substituted, especially in instructional laboratories. As we have already noted (p. 179) platinum crucibles must not be used in certain cases because of the danger of injury.

---

[1] When opening the desiccator after the crucible has cooled, the cover should be shoved aside slowly to avoid violent inrush of air.

[2] As noted elsewhere in this book, constant weight is denoted by two successive weighings differing by not more than 0.2 mg. in the usual case.

When platinum is heated at high temperatures — as with a Meker burner, a blast lamp, or in a muffle furnace — the slow loss in weight that it undergoes (p. 178) must be taken into account. The loss in weight may be allowed for by running a blank, i.e., heating the empty crucible at the same temperature and for the same period of time as in the ignition itself, and finding the change in weight. Or, if the platinum is not attacked in the slightest by the substance which has been ignited in it, the crucible may be cleaned after the ignition and reweighed; naturally, the solvent used to remove the adhering ignited residue must not affect the platinum at all, and mechanical cleaning (as with sand) is out of the question. It may also be mentioned here that in exact work the weight constancy of porcelain crucibles should be checked by blanks.

Drying and ignition of precipitates in filter crucibles. It is sometimes possible to dry a precipitate that has been collected in a filter crucible by passing successive small portions of alcohol and then ether,[1] or acetone alone, through the latter after the washing with water or aqueous solution has been completed. The crucible is then allowed to stand in the air or in a desiccator for a short time to allow the evaporation of the last traces of ether and water. This method of drying at room temperature gives good results with certain precipitates which are not finely divided and which do not adsorb or occlude appreciable amounts of water. However, it is not generally applicable. In most cases a precipitate must be heated to expel all the water.

When drying at low temperatures, the filter crucible is sucked as free from water as possible (often one or two rinsings with acetone is advantageous) and placed in a small beaker loosely covered with a watch glass to keep out dust. The beaker is placed in an electrically heated drying oven adjusted to the proper temperature. The first period of heating should be from an hour to an hour and a half in the usual case. Subsequent heatings to constant weight may be limited to half-hour periods.

For heating precipitates in filter crucibles at higher temperatures, an electric muffle furnace is preferably used. However, a flame may also be used. In the latter case the covered filter crucible is set in an ordinary porcelain crucible or capsule; filter crucibles must not be heated directly over the flame of a burner. If the precipitate is moist, heating must be gradual at first until the water is expelled.

---

[1] When the humidity is fairly high, there is danger of condensation of water vapor as a result of the rapid cooling.

CHAPTER XV

ERRORS IN QUANTITATIVE ANALYSIS

> *Suche die Methode der Analyse aufzufinden, bei welcher die Genauigkeit des Resultats am wenigsten von der Geschicklichkeit des operierenden Chemikers abhängt, und wenn diese ausgewählt ist, so sinne nach, welche unvermeidlichen Umstände vorhanden sind, die das Resultat unrichtig machen und ob es durch sie vergrössert oder verringert wird. . . .* — J. J. Berzelius (1814).

Aside from the theoretical impossibility of expressing the exact value of a physical quantity because of the incommensurability of the quantity measured and the unit in which it is expressed, there is, as anyone knows who has attempted exact measurement, a decided limit to the exactness with which any observation or measurement can be made. When a quantity is measured with the greatest exactness that the instruments and method are capable of and with the greatest care and skill that the individual can exercise, it is found that the results of successive measurements will differ among themselves to a greater or less extent. Evidently not all, and perhaps none, of the values obtained are correct within the possible limits of measurement. The average value of a series of measurements is accepted as the most probable. The average value will not usually be the true value. In some cases the difference between the two will be very small, and in others it may be so large that the result is unacceptable. After a measurement, or series of measurements, has been made, the question of the reliability of the result still remains to be considered. A quantitative chemical analysis is often a complex matter; it is subject to many possible errors, some physical and some chemical in nature, and it is by no means easy to obtain satisfactory results in all cases. The errors to which an analysis is subject must be evaluated and their influence on the final result considered.

In the following pages we shall consider the factors that affect the reliability of a quantitative chemical analysis and discuss methods of testing and increasing the accuracy of analyses.

Accuracy and precision.

At the outset it is necessary to define the term *error* and to distinguish between the terms *accuracy* and *precision,* which are often used interchangeably and therefore incorrectly.

The error of a measurement is the difference between the observed or measured value and the true value of the quantity measured:

$$E = O - T$$

where

E = absolute error
O = measured value
T = true value.

It is evident that the error of a measurement cannot be stated if the true value of the quantity is not known; and since the true value is established by measurement, it might seem impossible to find the error associated with any measurement, and this is indeed true in the strict sense of the term. The difficulty is, however, not insurmountable as far as practical requirements are concerned, as we shall show later.

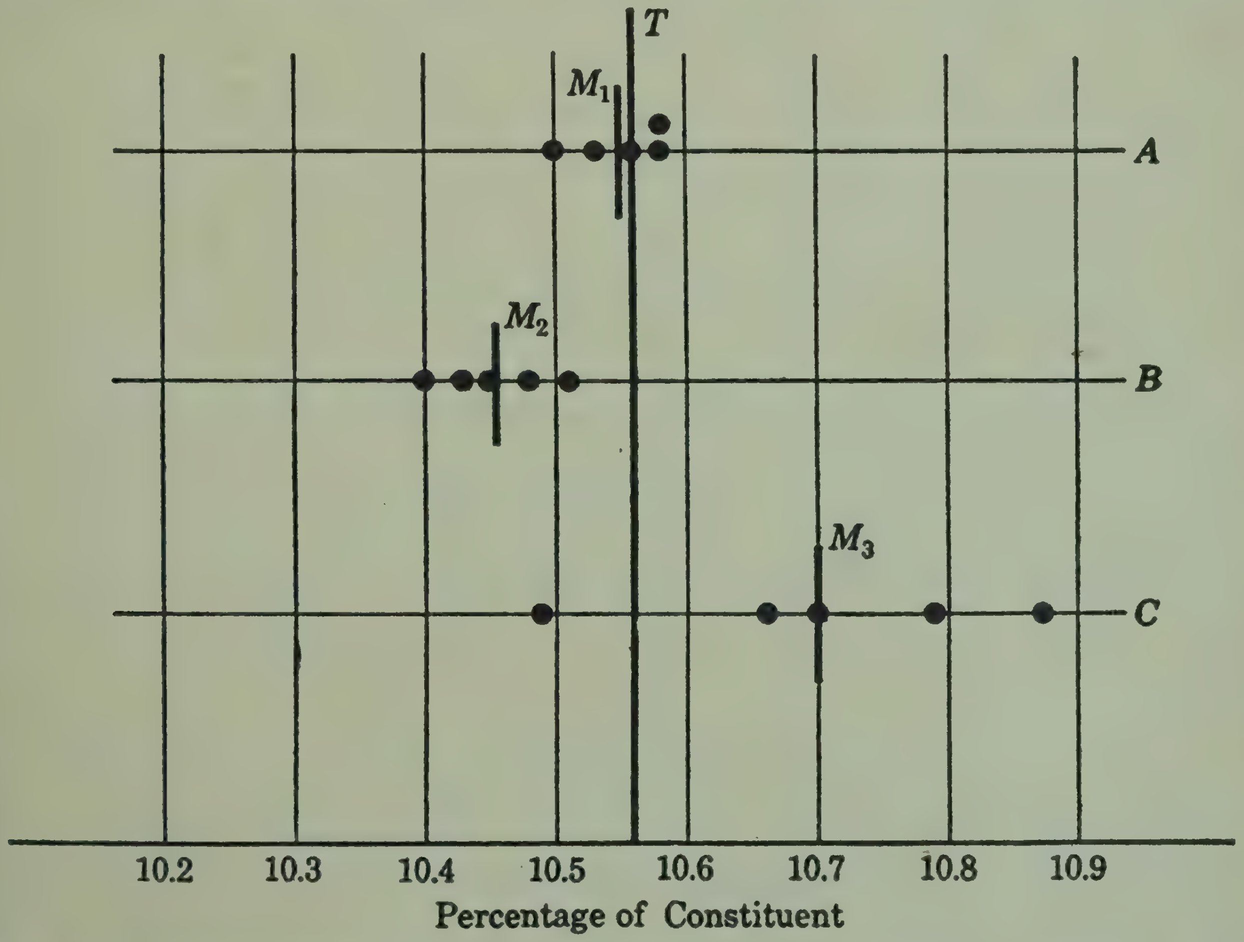


Fig. 67. Illustrating accuracy and precision in quantitative analysis. (Redrawn from Benedetti-Pichler, Ind. Eng. Chem., Anal. Ed. *8*, 373 (1936).)

The error of a measurement, E, is a measure of the *accuracy* of that measurement. Errors are not usually expressed in absolute values (as in the preceding formula), but in relative values, i.e., with respect to the true value, T, because the value of E without regard to the value of T is of no practical importance. Therefore it is in the value of $\frac{E}{T}$ that we are interested. This is the expression for *relative error.* It is convenient to express relative error in terms of percentage, $\frac{E}{T} \times 100$, or in parts per thousand, $\frac{E}{T} \times 1000$. The accuracy of a measurement is given by stating the relative error.

In those cases in which the true value of a quantity is not known with any degree of exactness, it is necessary to express the exactness of a measurement in some way that does not involve a knowledge of the error. This may be done by obtaining the arithmetical mean of a number of measurements and finding the difference between the value of a given measurement and the average value. This difference may be called the *deviation* of that particular measured value:

$$D = O - M$$

where

D = absolute deviation
O = measured value
M = arithmetical mean of measurements.

The magnitude of the deviations of a series of measurements is a measure of the *precision* of measurement. To have any practical significance, the value of the deviations must be expressed in relative figures with respect to M. The precision of a single observation then is $\frac{D}{M} \times 100$, expressed in percentage, or $\frac{D}{M} \times 1000$, in parts per thousand.

It is seen, then, that accuracy expresses the correctness of a measurement, and precision the reproducibility of a measurement. Accuracy without precision is obviously impossible, but precision does not by any means imply accuracy. The arithmetical mean of a number of measurements does not usually give the true value of the quantity measured, and there may be a considerable difference between the two. See Fig. 67.

Not until the true value of the quantity measured has been obtained, can the accuracy of the measurements be stated. Since the true value, T, must be found experimentally in the case of a physical or chemical quantity, its exact value must forever remain unknown; and therefore it is impossible, in the strict sense of the word, to find the accuracy of a measurement or method of measurement. However, it is quite possible in many instances to determine T with such accuracy that it can be stated the true value lies with overwhelming probability in a narrow range of which the carefully measured value is the center. Thus, suppose it is required to determine the probable accuracy of a method for the gravimetric determination of chloride in a given material. The method employed involves the precipitation of chloride as silver chloride under appropriate conditions, and the weighing of the dried precipitate. The chief errors which must be considered are the solubility of silver chloride, the presence of foreign substances in the weighed precipitate, and the slight uncertainty introduced by errors in weighing. Now, it is possible to correct the final result by determining the magnitude of the various errors. Thus, the amount of silver chloride which escapes precipitation can be determined (by methods with which we need not concern ourselves here). The correction value is found to be, let us say, $+ (a \pm a')$, where a' is the probable uncertainty of the value; a' is small compared to a. The correction for water and other contaminating substances in the weighed precipitate is $- (b \pm b')$. The uncertainty of all the weighings is $\pm c'$. The corrected value of O is then $O + a - b$ with the uncertainty $a' + b' + c'$. It can then be said that the value of T lies somewhere in the region $(O + a - b) \pm (a' + b' + c')$. The error of the measurement O is accordingly:

$$E = O - T = O - (O + a - b) \text{ with the uncertainty } \pm (a' + b' + c').$$

From the foregoing discussion it is plain that we are justified in certain cases in using the expressions *error* and *accuracy* in their strict sense when speaking of the reliability of measurements. If the range in which T is likely to fall is very small, compared to the difference between M and T, it is quite permissible to speak simply of the accuracy of measurement without qualification. Thus, if the true percentage of a constituent is known to lie in the range 10.06–10.08 per cent and the mean value obtained by a number of determinations is 10.17 per cent, it may be said that the accuracy of the determinations corresponds to an error of 0.10 per cent absolute.

Classification of errors.

In studying the errors that can be made in any measurement, it is advantageous to divide them into two classes:

1. Determinate errors.
2. Indeterminate or accidental errors.

Determinate errors. As the name implies, determinate errors are those which can be avoided, or whose magnitude can be determined and the measurements thereby corrected. A determinate error may have the same value under a variety of conditions and may remain constant from one measurement to another; such a determinate error is called a *constant* error. The presence of an impurity in a substance used for the standardization of a volumetric solution would be a source of a constant error; inaccuracies due to uncalibrated weights would fall in the same category (if the same pieces of weights were always used in successive weighings). Other determinate errors, on the other hand, will vary in magnitude and even in sign with the conditions. However, the law of the change may be known, so that the value of the error can be determined under any circumstances. Thus the expansion and contraction of volumetric solutions with a change in temperature give rise to variable errors; but the magnitude of the change can be determined by noting the temperature, since the coefficient of expansion of the solution (and glass) is known. These variable determinate errors are termed *systematic* errors.

The determinate errors that must be considered in chemical analysis are rather numerous. No attempt will be made here to enumerate them all, but the following list is suggestive; the more important ones are included. Four general classes may be distinguished:

(1) *Instrumental errors and those due to reagents.*

(a) Balance and weights. — These include: unequal arm lengths (not always a source of error), insufficient sensitivity, use of uncalibrated weights, etc.

(b) Volumetric apparatus. — Use of uncalibrated glassware.

(c) Vessels and utensils. — Introduction of foreign material through attack of glassware, porcelain, etc. Loss in weight of platinum crucibles when strongly heated.

(d) Reagents. — Presence of impurities, either the same as the substance sought or interfering substances.

(2) *Operative errors.* These errors are mostly physical in nature and are associated with the manipulations of an analysis. They are independent, to a great extent, of the instruments and utensils employed, they are not related at all to the chemical properties of the system in hand, and their magnitude depends more upon the analyst himself than on any other factor. Operative errors may assume serious proportions if the analyst is inexperienced, careless, or thoughtless. These errors are reduced to insignificance by careful, skillful, and understanding work. The following operative errors may be cited as typical: leaving vessels uncovered and thus introducing dust and other foreign material into solutions, spilling of liquids and solids, loss of material from solutions by effervescence and "bumping," failure to remove precipitates

quantitatively from vessels, loss in transfer of precipitates to the filter paper, underwashing or overwashing of precipitates, use of vessels of unsuitable size, placing crucibles in the wrong position when heating so that the flame gases gain access to the interior, insufficient time of heating or the use of improper temperatures in igniting precipitates, weighing of crucibles before they are completely cold, failure to guard against absorption of moisture by the substance weighed, failure to apply weight corrections, failure to apply temperature corrections in volumetric analysis, errors in calculations, use of nonrepresentative sample, etc. When such errors are due to carelessness, they are inexcusable. At first the beginner will be lacking in skill and understanding, and he may make more or less serious operative errors, often being unaware of so doing. Soon, however, he gains the necessary dexterity and insight, and his operative errors will then assume negligible proportions. The errors inherent in certain manipulations can never be entirely eliminated, but they can be reduced to such a small magnitude by the proper procedure that they will hardly come into consideration.

(3) *Personal errors.*

(a) Personal equation. — Somewhat different from the operative errors are the personal errors of the analyst; these have their source in the constitutional inability of an individual to make certain observations accurately. For example, some persons are unable to judge color changes exactly in titrations and may, for example, always go a little past the end point.[1] These errors are likely to be quite constant in magnitude; they are included in the "personal equation" of the observer.

(b) Prejudice. — When it is a question what tenth of a division is to be taken in reading a scale, the observer is likely to choose the one that will make the result agree more closely with the preceding one; if there is some doubt as to the exact location of the end point, the individual is apt to stop the titration at the point which will give a result in agreement with the previous titration if he knows what the buret reading should be for agreement, and so on. These are errors due to prejudice. Even conscientious workers may be influenced unconsciously by prejudice, and others unfortunately are only too willing to avail themselves of an excuse to make results agree, without gaining anything thereby.

---

[1] Color-blindness is a more serious form of such inability.

(4) *Errors of method.* These errors have their origin in the *chemical* or *physico-chemical* properties of the system in hand. They are by far the most serious errors encountered in chemical analysis. The errors enumerated above can be eliminated or reduced to very small magnitude by the proper technique, because they are mostly physical in nature. It is otherwise with the *methodic* errors; these are inherent in the method, and no matter how skillfully and carefully the analyst works, their magnitude remains the same unless the conditions of the determination are altered.

Some sources of methodic errors are these:

1. Solubility of a precipitate in the solution in which it is precipitated, and in the wash liquid.
2. Failure of a reaction to proceed to quantitative completion.
3. Precipitation of another substance with the reagent used.
4. Coprecipitation and postprecipitation.
5. Decomposition or volatilization of a precipitate on heating; hygroscopicity of the weighing form.
6. Induced reactions and side reactions.

Of course it is impossible to differentiate sharply between errors of operation and errors of method. Theoretically at least, methodic errors are operative errors in the sense that adoption of a better mode of procedure would eliminate or diminish the error. Some methodic errors might be classed as operative, as for example the decomposition of a precipitate on heating, if the range of stability is wide, so that the analyst can easily regulate the temperature to prevent decomposition. The solubility of a precipitate in a wash liquid may lead to no sensible error if the washing is properly done, whereas a significant error may be made if the amount of liquid used is excessive. Errors due to coprecipitation may in many cases be reduced to negligible proportions by dissolving the contaminated precipitate and reprecipitating it. In some cases it is difficult or practically impossible to alter the conditions so that better results can be obtained, and then the errors may be called methodic in the true sense of the word. From the standpoint of the student it is well to distinguish between methodic and non-methodic errors. For operative errors greater than an irreducible minimum, the student must be held responsible; methodic errors are no fault of his.

The methodic errors of common determinations will be considered in detail in the following chapters in the discussion of the respective procedures. Here it need only be emphasized that errors of method constitute the most serious source of inaccuracy in quantitative methods, because they often are very difficult to eliminate.

A few words may be said about *additive* and *proportional* determinate errors. An additive error is one which has the same absolute value no matter what the amount of the constituent being determined, while a proportional error is one whose absolute magnitude depends upon the quantity of the constituent. Benedetti-Pichler[1] gives an instructive example dealing with a method for aluminum involving precipitation of the hydroxide with ammonia and ignition of the washed precipitate to the oxide at a high temperature. In the first series of experiments the following amounts of aluminum oxide were obtained from the indicated amounts of potassium alum:

K ALUM	Al_2O_3 FOUND	Al_2O_3 TAKEN	DIFFERENCE
g.	g.	g.	g.
1.0000	0.1288	0.1077	+ 0.021
2.0000	0.2384	0.2154	+ 0.023
3.0000	0.3489	0.3231	+ 0.026
4.0000	0.4588	0.4308	+ 0.028
Blank	0.000	0.000	+ 0.000

It will be seen that the errors (values in the last column) are nearly constant; they show only a slight increase as the amount of aluminum is increased 400 per cent. The major portion of the error was found to be due to silicic acid in the ammonia, which was coprecipitated nearly completely with the aluminum hydroxide. Since practically the same volume of ammonia was used in each determination, it is evident why the error due to silica should be additive.

In the second series of experiments freshly distilled ammonia was used in the precipitation, and the following results were obtained:

K ALUM	Al_2O_3 FOUND	Al_2O_3 TAKEN	DIFFERENCE
g.	g.	g.	g.
1.0000	0.1087	0.1077	+ 0.0010
2.0000	0.2178	0.2154	+ 0.0024
3.0000	0.3258	0.3231	+ 0.0027
4.0000	0.4352	0.4308	+ 0.0044

The errors here are clearly proportional, amounting to about 10 parts per thousand. The high results are due to the presence of water in the ignited residue; even after strong ignition aluminum oxide may retain water (p. 325). It is now apparent that the errors of the first series are actually a composite of additive and proportional errors, the former predominating.

This example illustrates how valuable an analysis of errors may be in locating the source of inaccuracies in a method. Moreover it shows that in testing a method one should always take various amounts of sample in order that the possible presence of additive and proportional errors may be revealed.

---

[1] A. A. Benedetti-Pichler, Ind. Eng. Chem., Anal. Ed. *8*, 373 (1936).

Indeterminate or accidental errors. The existence of another class of errors, called indeterminate or accidental, is revealed by the small differences in the successive values of a measured quantity when the measurements are made by the same person with great care under conditions as nearly the same as possible. Indeterminate errors cannot be allowed for or corrected in the same manner as determinate errors, because the cause and law of variation of the former are unknown; indeed indeterminate errors appear to follow no law.

It is generally stated that accidental errors are beyond the power of the observer to prevent or allow for, but it should be understood that this statement refers to unchanging conditions and methods of measurement. By working under slightly different conditions and by taking certain precautions, or by adopting a different mode of procedure, it may be possible to reduce the variations in successive measurements to the point where they are no longer of significance. The weighing of a hygroscopic substance provides an illustration. Suppose an analyst is unaware of or underestimates the hygroscopic nature of a substance and weighs it after successive dryings in obtaining constant weight. He will find the observed weights to be variable, the exact weight in any weighing depending upon the time required to make the weighing (which determines the amount of moisture taken up by the substance) and perhaps upon the variable humidity of the atmosphere. To him the variable results may appear inexplicable, and he will attribute the variations to accidental errors. Actually these variable values are only the result of variable determinate errors. A practiced analyst would at once ascribe the variability in weight to the hygroscopic nature of the substance and would make the weighings under conditions such that the absorption of moisture would be impossible or difficult. The discrepancies would then disappear or assume a trifling magnitude. It is apparent that indeterminate errors have their origin in the limited ability of the observer to control conditions or to make corrections for changes in external conditions, or to his inability to recognize the appearance of new factors.

Even though corrections cannot be applied to counteract the effect of accidental errors, it is possible to come to some conclusion regarding the most probable result of a series of measurements. The answer to the problem is obtained by the application of certain mathematical considerations based on the theory of probability. It is beyond the scope of this book to enter into the mathematics of the problem, especially since the rigorous application of the mathematical formulas obtained is rarely possible, and unnecessary as well, in ordinary quantitative work. However, every analyst should know something about the general methods of obtaining the most probable value of a series of measurements and the degree of its reliability, and therefore the matter is briefly considered here.[1]

In studying indeterminate errors the following assumptions are made:

1. Positive and negative deviations of the same magnitude are equally probable.
2. The probability of a small deviation is greater than the probability of a large deviation.
3. Very large deviations are very unlikely to occur.

By mathematical analysis it is found that the following relation exists between the frequency of a deviation and its magnitude:

$$y = \frac{h}{\sqrt{\pi}} e^{-h^2x^2}$$

in which

y = frequency of occurrence of a deviation
x = magnitude of deviation whose frequency is y
h = constant (value depends upon character of measurements).[2]
π and e have the usual meaning.

Figure 68 represents the curve of this equation, which is called the probability curve or the error curve. It is seen that positive and negative deviations are equally probable and that small deviations occur more frequently than large ones; this is in accord with experience. The ideal curve represented is based upon an infinite number of observations. The greater the number of observations, the more closely the deviations will be represented by the probability curve.

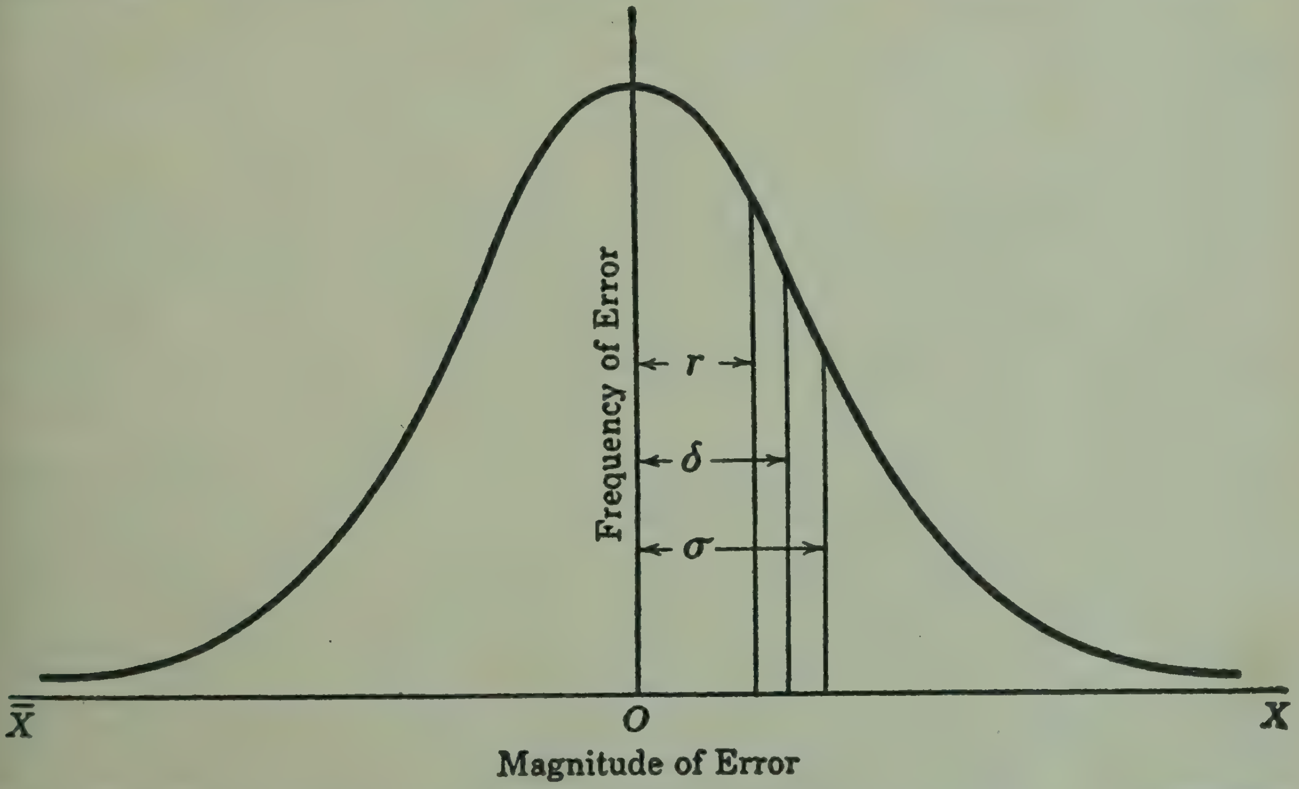


FIG. 68. The normal error curve. δ = average deviation, σ = standard deviation, and r = probable deviation.

---

[1] For a detailed treatment see T. B. Crumpler and J. H. Yoe, *Chemical Computations and Errors*, John Wiley and Sons, New York, 1940.

[2] $h = \dfrac{1}{\sqrt{2} \times \text{standard deviation}}$

The error curve justifies graphically the choice of the arithmetical mean as the most probable value of a number of observations, because it is seen that the curve is symmetrical with respect to the y-axis. Fundamentally, the choice of the arithmetical mean is based upon the assumption that positive and negative deviations of the same magnitude are equally probable, and this assumption is verified by experience. The greater the number of observations, the closer will the arithmetical mean approach the most probable value. If the number of observations is few, it is clear that there may be a considerable difference between the two, especially if the precision of measurement is low. This limitation must always be borne in mind. Furthermore, it must be realized that the arithmetical mean will correspond to the true value of the measured quantity only when there are no determinate errors in the method. Referring again to Figure 67, we see that the arithmetical mean M does not give the true value T. The deviations from M represent the indeterminate errors, and the difference between M and T represents the determinate error or sum of errors, which was not or could not be allowed for in the analysis. *Only when we have some assurance that the variations are occurring on both sides of the true value, are we justified in attaching any significance to the arithmetical mean.* Many of the errors of quantitative analysis are of such a nature that they always have the same sign. Thus, in weighing a hygroscopic substance as in the example above, we can obtain a result that is too high but never one that is too low. If a hygroscopic substance has been weighed successively after drying and a number of values of its weight accumulated, the arithmetical mean of the slightly different results will give a value which is more in error than the lowest result of the series of weighings. Similarly, in removing a precipitate from a precipitating vessel, we can err in defect but never in excess. In such cases we are dealing with pseudo-accidental errors, which are really only variable determinate errors that have a definite limit. It is important, therefore, to differentiate between true accidental errors which can assume both positive and negative values with respect to the true value and the seemingly indeterminate errors which have a fixed sign. In some cases we are unable to determine whether the variations are "one-sided" or not, and then we are forced to accept the arithmetical mean as giving the most probable value, for the want of anything better. If an analysis consists of a long series of operations, it is quite probable that even if many of the deviations are "one-sided" the average result will be quite close to the truth, because some of the deviations will have positive one-sidedness and others negative, and thus there may be compensations. The extent of the compensation will depend upon the number of variations and their relative values. If one step involves a one-sided variation larger than any of the others, we are justified in laying more weight on a result slightly higher or lower than the arithmetical mean, as the case may be; and by appropriate means it is even possible to determine the approximate value of the variation and correct the mean accordingly. Looked at in another way, the last step consists in nothing else but finding the most probable value of a variable determinate error; and here the law of probability may be used.

Assuming then that the accidental errors of a series of measurements follow the law of probability, it becomes highly desirable to find an expression for the magnitude of the accidental error[1] attached to the arithmetical mean. It can be shown that the arithmetical mean derived from n measurements is $\sqrt{n}$ times as reliable as a single measurement. If the uncertainty of a single measurement is u, the uncertainty of the mean is accordingly

$$\frac{u}{\sqrt{n}}.$$

The precision of a measurement of a series made under the same conditions may be expressed in several different ways; namely, by the average deviation, the standard deviation, and the probable deviation.

The measure of precision most commonly used in ordinary chemical analysis is the *average deviation of a single measurement*, which is defined as the mean of the differences between the measured values and the arithmetical mean without regard to sign:

$$\frac{|d_1| + |d_2| + \cdots |d_n|}{n}.$$

The *standard deviation of a single measurement* is defined as the deviation whose square is the mean of the squares of the differences between the measured values and the arithmetical mean:

$$\sqrt{\frac{d_1^2 + d_2^2 + \cdots d_n^2}{n}}.$$

If the number of measurements is small, a better approximation to the standard deviation is obtained by the use of the formula:[2]

$$\sqrt{\frac{d_1^2 + d_2^2 + \cdots d_n^2}{n - 1}}.$$

The standard deviation is a better measure of precision than the average deviation because it takes the dispersion of the deviations into account.

The *probable deviation of a single measurement* is the deviation that has a magnitude such that in an infinite number of measurements the number of deviations having values greater than it will be equal to the number having values smaller than it. The expression for the probable deviation is:

$$0.67\sqrt{\frac{d_1^2 + d_2^2 + \cdots d_n^2}{n - 1}}.$$

---

[1] We are here using the term *error* in its wider general sense and not in the strictly accurate sense defined by the equation $E = O - T$.

[2] The theoretical standard deviation is based on a very large number of measurements. If the number of measurements is small, the calculated mean may diverge considerably from the true mean; and to allow for this, the factor $\frac{1}{n-1}$ is used in place of $\frac{1}{n}$.

In the normal error curve the probable deviation is represented by the abscissa of the line dividing the area under the curve in the quadrant XOY (or $\overline{X}OY$) into two equal parts (Fig. 68).

When n is large and the distribution of deviations follows the normal error curve, the following relations exist between the three precision measures: average deviation = 0.80 standard deviation = 1.18 probable deviation.

The precision of the arithmetical mean may be expressed as:

$$\text{Average deviation of the mean} = \frac{\text{average deviation of a single measurement}}{\sqrt{n}}$$

$$\text{Standard deviation of the mean} = \frac{\text{standard deviation of a single measurement}}{\sqrt{n}}$$

$$\text{Probable deviation of the mean} = \frac{\text{probable deviation of a single measurement}}{\sqrt{n}}.$$

EXAMPLE. Five careful determinations of iron in an iron ore by a volumetric method yielded the percentages 67.48, 67.37, 67.47, 67.43, and 67.40. Find the average deviation, standard deviation, and probable deviation of a single determination and of the mean.

ANSWER:

PERCENTAGE	d	d^2
67.48	0.05	0.0025
67.37	0.06	0.0036
67.47	0.04	0.0016
67.43	0.00	0.0000
67.40	0.03	0.0009
Mean = 67.43	Σd = 0.18	Σd^2 = 0.0086

Average deviation of a single determination $= \dfrac{0.18}{5} = 0.036$ per cent absolute or 0.5 part per thousand

Standard deviation of a single determination $= \sqrt{\dfrac{0.0086}{4}} = 0.047$ per cent absolute or 0.7 part per thousand

Probable deviation of a single determination $= 0.67 \times 0.047 = 0.031$ per cent absolute or 0.5 part per thousand

Average deviation of the mean $= \dfrac{0.036}{\sqrt{5}} = 0.016$ per cent absolute or 0.24 part per thousand

Standard deviation of the mean $= \dfrac{0.047}{\sqrt{5}} = 0.021$ per cent absolute or 0.31 part per thousand

Probable deviation of the mean $= \dfrac{0.031}{\sqrt{5}} = 0.014$ per cent absolute or 0.21 part per thousand.

(The deviations of a single measurement and of the mean expressed in parts per thousand should usually be rounded off to the first decimal unless the values are to be used in calculations.)

For the ordinary purposes of quantitative analysis, the precision may be expressed by giving the average deviation of a single measurement. Thus, in the above example the precision of the analyses is described sufficiently well by stating that the average deviation of a determination is 0.5 part per thousand.

The accuracy of a result can be increased as far as accidental errors are concerned by increasing the number of measurements. However, the deviation of the mean does not decrease in the ratio of the number of measurements but as the square root of the number, as we have already seen. Therefore a point is soon reached when the slight increase in precision that can be attained by making more measurements does not justify the expenditure of the time and labor required. If the deviation of the mean of n determinations is U, the theoretical deviation of $2\,n$ determinations will be $0.71\,U$, of $3\,n$ determinations $0.58\,U$, etc. (see Fig. 69).

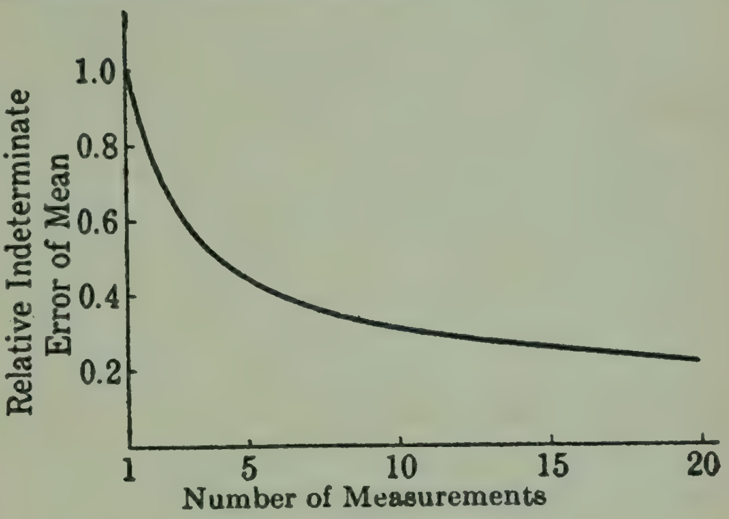


FIG. 69. Precision of the mean as a function of the number of measurements.

TABLE XLIII. PROBABILITY OF DEVIATIONS IN TERMS OF THE PROBABLE DEVIATION

(P = probability that deviation will fall in the range $\pm x$; r = probable deviation.)

x/r	P	x/r	P
0.1	0.0538	4.4	0.9970
0.5	0.2641	4.5	0.9976
1.0	0.5000	4.6	0.9981
1.5	0.6883	4.7	0.9885
2.0	0.8227	4.8	0.9988
2.5	0.9082	4.9	0.9990
3.0	0.9570	5.0	0.9993
3.5	0.9818	5.1	0.9994
4.0	0.9930	5.2	0.9996
4.1	0.9943	5.3	0.9997
4.2	0.9954	5.4	0.9997
4.3	0.9963	∞	1.0000

If a sufficiently large number of measurements has been made so that the probable deviation is known with some degree of certainty, it is possible to predict the probability of the occurrence of a deviation between the limits $+x$ and $-x$ by making use of Table XLIII, which gives the probability corresponding to various values of $\frac{x}{r}$ (r is the probable deviation). Normal distribution of deviations is assumed. Some illustrations of the use of this table will be given later.

Rejection of a result. It sometimes happens that one result of a series of measurements of the same quantity differs considerably in value from the others. If all the measurements have been made with equal care, the question arises whether the doubtful value may be rejected even if one is not aware of having made an error in obtaining the divergent result. This question may be answered in the affirmative, for it can be readily shown from the mathematical theory of errors that if the deviation of the dubious result from the mean exceeds a certain critical value the probability is small that it is a true member of the series. In other words, a large deviation is not likely to be due to chance, i.e., to the fortuitous combination of many small inherent errors all of the same sign, but instead to an unknown determinate error, for example. Thus a high result in a series of gravimetric determinations might be due to some foreign material falling into the crucible containing the precipitate to be weighed.

The extent to which a divergent result must depart from the average to qualify it for rejection is partly a matter of opinion, and various authors give various criteria. For general use in quantitative analysis, we have adopted the criterion of a number of statistical writers[1] who regard a result as being sufficiently discrepant for rejection *if its deviation from the arithmetical mean exceeds twice the standard deviation of a single measurement.* A result having a deviation as large as this has a probability of about 0.045 (cf. Table XLIII). In other words, in a thousand measurements only 45 would be expected to show random deviations as large as this. This means that the odds are 21 against 1 that an error of this magnitude is due to chance alone.[2]

Since the standard deviation of a single measurement is in the limit equal to 1.25 × *average deviation*, we may for most practical purposes express the critical ratio for the rejection of a result as:

$$\frac{\text{deviation of doubtful result}}{\text{average deviation}} > 2.5.$$

We then have the following rule regarding the rejection of a doubtful result in a series: *Calculate the arithmetical mean and the average deviation, omitting the suspected result. Divide the deviation of the doubtful result by the average deviation. If the quotient is greater than 2.5, reject the doubtful value.* At least four results must be available before this rule can be applied. With less than this number the average deviation must be obtained from but two results and will be too uncertain to allow any conclusions to be drawn.

---

[1] See, for example, R. A. Fisher, *Statistical Methods for Research Workers*, 5th ed., p. 44, Oliver and Boyd, London, 1934. F. W. Power, Ind. Eng. Chem., Anal. Ed. *11*, 662 (1939), has applied this criterion in a study of the accuracy and precision of the microanalytical determination of carbon and hydrogen.

[2] It will be evident that the criterion of rejection should not be a constant but should depend upon the number of measurements made. Thus the criterion we have adopted is not valid if a large number of measurements has been made. In a series of 22 measurements, one result will normally show a deviation equal to, or larger than, twice the standard deviation. The criterion of Chauvenet (see Mellor, *Higher Mathematics for Students of Chemistry and Physics*) takes the number of measurements into account. Our criterion is satisfactory for most cases encountered in quantitative analysis, in which relatively few parallel determinations are involved.

Example. Four determinations of chlorine in a sample of chloride yielded the values 30.34, 30.22, 30.42, and 30.48 per cent Cl. Should any of the results be rejected?

Evidently 30.22 is the doubtful value. The arithmetical mean is 30.41, the average deviation is 0.05, and the deviation of the doubtful result is 0.19. Since $\frac{0.19}{0.05} = 3.8$, the value 30.22 should not be included in the average.

The conclusion that is drawn by the application of this test cannot be regarded as very certain, chiefly because the average deviation is obtained from few measurements in most cases and it may therefore differ considerably from the true average deviation. When a suspicious result appears in a limited series of measurements, the best policy is to make more measurements. If this is not practicable, the next best procedure is to apply the test just given. In the long run this test excludes the majority of results which should not be included in the average, without rejecting those that should be included.[1]

Error in a derived result. The final result of an analysis is nearly always derived from the measurement of more than one quantity, and the important question arises: What will be the error in such an indirect result calculated from a number of quantities, each having a certain known or possible error or deviation? The answer to this question has been succinctly stated by Benedetti-Pichler [2] in the form of a little table which is given below (Table XLIV).

Table XLIV. Error in a Derived Result

R = final result

A, B, C = measured quantities from which R is derived

r, a, b, c = absolute errors (or deviations) of R, A, B, C, respectively

r_r, a_r, b_r, c_r = relative errors of R, A, B, C, respectively

	R calculated as sum or difference $(R = A + B - C)$	R calculated as product or quotient $\left(R = \frac{AB}{C}\right)$
Determinate errors —	$r = a + b - c$	$r_r = a_r + b_r - c_r$
Indeterminate errors —	$r = \pm\sqrt{a^2 + b^2 + c^2}$	$r_r = \pm\sqrt{a_r^2 + b_r^2 + c_r^2}$

---

[1] A criterion of rejection sometimes given specifies that a result should not be discarded unless its deviation from the mean exceeds four times the average deviation. The probability of the occurrence of a deviation of this size is 0.0014, which means that the chances against its legitimate occurrence are approximately 700 to 1. This test allows the inclusion of a result that is likely to be in error, and the use of such a value in obtaining the average is open to as much objection as the unjustified rejection of a result. It may further be observed that in a limited series of measurements one is justified in excluding from the mean a measurement which shows a moderately large deviation even if it be a valid member of the series, since it has an undue effect on the mean if included.

[2] A. A. Benedetti-Pichler, Ind. Eng. Chem., Anal. Ed. *8*, 376 (1936).

The truth of the formulas in this table is practically self-evident. A few examples may be given.

Example 1. A sample absorbed 1 per cent of water during weighing, the precipitate was contaminated with 2 per cent of a coprecipitated substance unchanged on ignition, and the ignited residue contained 2 per cent of water. If the percentage of constituent found was 10.0 per cent, what is the error in parts per thousand and absolute per cent?

Ans. Error in p.p.t. $= -10 + 20 + 20 = +30$. Error in absolute per cent $= + \frac{30}{1000} \times 10 = +0.3$.

Example 2. If a single weighing may be in error by 0.0001 g., with what precision may the mass of a body be determined?

Ans. The error in question is an indeterminate one, and the mathematical theory of errors indicates that the precision of the result is given by $\sqrt{0.0001^2 + 0.0001^2} = \pm 0.00014$ g., because finding the weight of a body is actually a process of finding the difference between two weights (determination of the rest point of the empty and loaded balance).

Example 3. Assuming that the probable error of a single weighing is 0.0001 g., what is the probable error in the determination of chlorine in a 0.20 g. sample of chloride yielding a silver chloride precipitate weighing 0.25 g.?

Ans. Since we wish to express the error on the relative basis (p.p.t.), we have:

$$\begin{aligned}\text{Probable error} &= \pm\sqrt{(2 \times 0.5^2) + (2 \times 0.4^2)}\\ &= \sqrt{0.82} = \pm 0.9 \text{ or 1 part per thousand.}\end{aligned}$$

If it is desired to express the error in terms of the absolute percentage of chlorine, we have:

$$\text{Probable error} = 0.0009 \times \frac{\text{Cl}}{\text{AgCl}} \times \frac{0.25}{0.20} \times 100 = \pm 0.03 \text{ per cent.}$$

Sample size. A problem which is sometimes encountered in analytical work involves the size of sample that must be taken in order that the error (deviation) in the percentage of constituent found shall not exceed a specified amount, the indeterminate error in each of the measured quantities being known.

We shall approach the problem by finding the size of sample it is necessary to take in order that the average deviation of the percentage shall be a specified value. The percentage, P, of a constituent in a sample is given by the expression:

$$P = \frac{100\,FM}{S}$$

where F = chemical factor

M = *measure* of the constituent (weight of the weighing form in gravimetric analysis)

S = weight of sample.

The absolute average deviations of P, M, and S we shall designate by p, m, and s, and the relative average deviations of the same quantities by p_r, m_r, and s_r, respectively. The absolute average deviation of a single weighing will be denoted by w.

The relative average deviation of P in terms of the deviations of the quantities from which it is derived is given by:

$$p_r = \pm\sqrt{m_r^2 + s_r^2} \qquad \text{(See p. 277)}$$

$$= \pm\sqrt{\left(\frac{m}{M} \times 1000\right)^2 + \left(\frac{s}{S} \times 1000\right)^2} \text{ in parts per thousand} \qquad (1)$$

The preceding equation is a general one which can be applied in gravimetric, volumetric, etc. analysis. In gravimetric analysis this expression becomes:

$$p_r = \pm\sqrt{\left(\frac{1.4\,w}{M} \times 1000\right)^2 + \left(\frac{1.4\,w}{S} \times 1000\right)^2}$$

By substituting $\frac{PS}{100\,F}$ for M in the preceding equation and solving for S, we obtain:

$$S = \frac{1400\,w}{p_r}\sqrt{\left(\frac{100\,F}{P}\right)^2 + 1}. \qquad (2)$$

If $\frac{100\,F}{P}$ is $\lesseqgtr 0.5$, it may be disregarded in the equation;[1] and if $\frac{100\,F}{P}$ is greater than 2, the 1 under the square root sign may be disregarded.

The above expression then gives the weight of sample that must be taken in order that in the long run the average deviation of P in parts per thousand shall be $\pm\ p_r$ if the average deviation of a single weighing is w. Generally, however, the analyst desires to know the size of the sample that must be taken in order that it shall be a practical certainty that the deviation $\pm\ p_r$ shall not be exceeded in an analysis. It is evident that as the weight of sample is increased the relative accidental error of P decreases, or, otherwise expressed, the probability that a specified deviation will be exceeded is decreased as the size of sample is increased. It is a simple matter to obtain the odds that a specified deviation will not be exceeded with a specified weight of sample expressed in terms of S. From equation (2) we have

$$(p_r)_s = \frac{\text{constant}}{\text{weight of sample}}$$

in which $(p_r)_s$ is a deviation which is equal to the average deviation when the sample weight is S. The probability that a deviation will not exceed

---

[1] If R is derived from two measurements, A and B, and the relative indeterminate error of B is $\frac{1}{2}$ (or less) as great as that of A, one may as well forget about the error contributed by B, because the error in R will at the worst be only 12 per cent greater on account of the error in B

$$\left(\frac{\sqrt{1 + 0.5^2}}{\sqrt{1}} = 1.12\right).$$

the average deviation p_r with a sample of weight S is found by looking up the value $\frac{x}{r}$ in Table XLV, x being the deviation and r the probable deviation. Since the average deviation is $1.18\,r$, $\frac{x}{r}$ is 1.18, and the corresponding probability is found to be about 0.57. If the size of sample is increased to $2\,S$, we obtain a new relative average deviation $(p_r)_{2s} = \frac{(p_r)_s}{2}$. Since the probability of obtaining a deviation less than $(p_r)_{2s}$ with $2\,S$ is obviously the same as obtaining a deviation less than $(p_r)_s$ with S, the probability of getting a deviation within the limits $\pm\,(p_r)_s$ with $2\,S$ corresponds to $\frac{x}{r} = 2.36$, or a value of 0.889. Values for the probability of $(p_r)_s$ with samples of other sizes are given in Table XLV.

TABLE XLV. PROBABILITY THAT DEVIATION CORRESPONDING TO $\pm(p_r)_s$ WILL NOT BE EXCEEDED FOR VARIOUS SAMPLE WEIGHTS IN TERMS OF S

WEIGHT OF SAMPLE	PROBABILITY	ODDS
S	0.574	1.3 : 1
$2\,S$	0.889	8 : 1
$2.5\,S$	0.953	20 : 1
$3\,S$	0.983	58 : 1
$3.5\,S$	0.9946	184 : 1
$4\,S$	0.9986	713 : 1
$4.5\,S$	0.9997	3330 : 1

It is seen that if we take a sample four times larger than that which in the long run gives a specified average deviation it will be extremely unlikely that this deviation will be exceeded.[1] *This deduction is based on the assumption that the only accidental errors in the procedure are those of weighing.*

Determination of the accuracy and precision of a method. Analytical methods differ considerably in the accuracy and precision that they afford. The precision of a method is more easily determined than its accuracy. In a pure solution of a constituent both may be determined with little difficulty. The accuracy of a given method depends to a great extent upon the nature of the sample. In practical work the sample may be complex, separations may be required, and the accuracy of the final result may depend more upon the preliminary steps than on the final determination.

In establishing the precision and accuracy of a method, one takes a known amount of the constituent in the form of a carefully purified element or compound of definite composition. Since atomic weights are known with greater accuracy than any constituent can be determined by ordinary analysis, the true amount of the constituent present may be considered known. A series of determinations — from five to ten — are then run under specified conditions. The arithmetical mean of the results and the average deviation are calculated. The average deviation of a single determination may be used as a measure of the precision of the method. The difference between the mean and the theoretical value gives the constant error of the method.

---

[1] A. A. Benedetti-Pichler, Ind. Eng. Chem., Anal. Ed. *11*, 226 (1939).

The following example may be taken by way of illustration. Benedetti-Pichler[1] and co-workers investigated the gravimetric microdetermination of aluminum with 8-hydroxyquinoline by determining the element in from 1.7 to 6.5 mg. of $KAl(SO_4)_2 \cdot 12\,H_2O$. The following percentages of Al_2O_3 were found in nine determinations:

10.74	10.77	10.77
10.77	10.81	10.82
10.73	10.86	10.81

Arithmetical mean = 10.79 per cent Al_2O_3; average deviation = ± 0.034 per cent or 3 parts per thousand.
Average deviation of mean = 0.011 per cent (1 part per thousand).
True percentage = 10.77.

Instead of giving all the above data, the results of the investigation of the method may be summarized briefly as follows:[2]

Nine determinations of aluminum in pure $KAl(SO_4)_2 \cdot 12\,H_2O$ (1.7 to 6.5 mg. samples) with 8-hydroxyquinoline gave an average of 10.79 ± 0.011 per cent Al_2O_3(± 1 p.p.t.); theoretical value 10.77 per cent Al_2O_3.

The apparent constant error of the method amounts to + 2(± 1) parts per thousand. To determine whether the deviation of the mean from the theoretical value has any significance, we may apply the test described on p. 276:

$$\frac{\text{true value} - \text{value of mean}}{\text{average deviation of mean}} = \frac{2}{1} = 2.$$

The limit 2.5 is not exceeded, and there is therefore a fair chance that the deviation of the arithmetical mean from the true value is due to accidental errors. The presence of a constant error cannot be assumed.

The average deviation of a single determination can be obtained from the average deviation of the mean given in the statement above by multiplying by $\sqrt{9}$, i.e., $3 \times 0.011 = \pm\, 0.03$ per cent (± 3 p.p.t.). It may be expected that determinations made by the method in the future under the same conditions (including the same size of sample) will show an average deviation of 3 p.p.t. and that a deviation exceeding 12 p.p.t. will occur only once in about 700 times.

Accuracy sought in quantitative analysis.

What are the permissible limits of error in a quantitative chemical analysis? To this question it is impossible to give a simple all-inclusive answer. Primarily, the accuracy sought in any analysis is determined by the use to which the result is to be put or, in other words, by the importance attached to the result. Analyses which are made to find the values of certain constants of nature (atomic weights, for example) or to establish or prove laws of nature (for example, Faraday's laws) must obviously be made with the most painstaking care. Especially is this the case in the determination of atomic weights. These are of fundamental importance to pure science as well as to applied science. The accuracy of the atomic weights is of the greatest importance to quantitative analysis, because the accuracy of the results of nearly all analyses depends upon them.

---

[1] A. A. Benedetti-Pichler, *Mikrochemie*, Pregl Festschrift 6 (1929).

[2] A. A. Benedetti-Pichler, Ind. Eng. Chem., Anal. Ed. *8*, 374 (1936).

Next in order of accuracy come analyses in which an accuracy corresponding to an error of one part in a thousand is sought in the determination of those constituents which are present in fairly large amounts. In this class we have many scientific analyses (rock analysis, analyses to establish formulas of artificially prepared compounds and minerals, etc.), as well as many commercial ones. However, even in this class an error of a few tenths of a per cent (relative) and even greater errors are sometimes permissible.

Then there are other types of analyses in which a high degree of accuracy is not aimed at, because it is not required. Many determinations in food and physiological analysis, for instance, are entirely satisfactory if the results are within a few per cent of the truth. Obviously it is a waste of time and labor to determine a constituent with great accuracy, even when this is possible, if there is no particular demand for a very accurate result.

Generally speaking, the accuracy which can be attained in any analysis is a function of the time that can be placed upon the determination. By making double and triple precipitations in separations, for example, the accuracy can usually be increased greatly but only at the expense of extra time and effort. If one precipitation gives results of fair accuracy, it would be foolish to make reprecipitations unless the higher accuracy actually is needed. It is all a matter of common sense; the analyst must possess a sense of values. In this book special attention is paid to procedures which are capable of giving rather high accuracy. The analyst who can perform accurate analyses and who has a grasp of the factors involved in any analysis will understand what legitimate changes can be made in a procedure when results of lesser accuracy are satisfactory. We have in some cases attempted to show by means of tables the magnitude of the errors resulting when the recommended procedure is departed from.

In taking into account the factors which influence the degree of accuracy with which any constituent can be determined by any method, special attention must be paid to the substances which accompany the constituent and to the relative amounts of the latter present. Usually, pure solutions of substances offer no difficulty in analysis, and high accuracy is attainable if proper attention is paid to manipulative details. It is otherwise when the constituent in question is accompanied by others which may seriously interfere for reasons indicated elsewhere in this chapter. Thus, there is no particular difficulty in determining calcium accurately when it occurs in the form of a pure salt, but the matter is different when the element is accompanied by magnesium, as it usually is. Naturally, larger errors must be expected in the analyses of complex natural materials or artificial products than in academic analyses of pure solutions.

As already stated, it is usually the aim in ordinary careful analysis to obtain an accuracy corresponding to an error of one part per thousand in the determination of a constituent occurring in relatively large amounts in a sample. It is not possible to say exactly what the lower limit of percentage of constituent is which makes this accuracy reasonable to expect, because the value of the calculation factor (in gravimetric analysis) is an important deciding factor. In general, it may be said that it is unreasonable in most cases to expect the determination of a constituent making up 10 per cent of the sample to be accurate to one part in a thousand or to ± .01 absolute per cent. On the other hand, an error of one part in a hundred is in this case usually too large. The degree of accuracy sought should lie somewhere between these limits. For smaller amounts of constituents the accuracy which may be expected in general is shown in the following little table, in which x represents the digit which may be expected to vary:

Percentage Constituent in Sample	Permissible Variation Per Cent
1.00	$0.0x$
0.1	$0.0x$ to $0.00x$
0.01	$0.00x$
0.001	$0.00x$ to $0.000x$

Of course it should be understood that this table is suggestive merely. For constituents present in large amounts the size of the relative error is the important point, for moderately small amounts both the relative error and the absolute error must be taken into consideration, whereas for very small amounts the relative error as a rule becomes quite unimportant. In some cases, however, substances present in relatively very small amounts must be determined with small relative error as, for example, gold in an ore.

Substances present in a sample to the extent of 0.01 to 0.001 per cent cannot usually be determined sufficiently accurately gravimetrically because the sensitivity of the analytical balance is not much greater than 0.0001 g. This means that by taking a sample of the order of one gram it is useless to hope for an accuracy much greater than 0.01 absolute per cent on account of the limitation in weighing imposed. Actually other factors, such as the solubility of the precipitate or the effect of the relatively huge amounts of other substances, may prevent the attainment of even this accuracy. For very small percentages of constituent, volumetric and colorimetric methods are applicable, especially the latter. The relative error of colorimetric methods is large, being of the order of 2 to 5 per cent, but this is of small moment when the absolute amount of the constituent present is very small (0.1 to 0.001 per cent). Spectroscopic methods are of great value in determining extremely small amounts of substances (p. 691), although again the relative error is fairly large.

When only very small amounts of sample are available, micro methods

(p. 6) can be applied. Using micro technique, samples one-hundredth as large as the ordinary macro samples can be analyzed with approximately the same accuracy as the latter.

Methods of checking the accuracy of analyses.

Parallel determinations. The results obtained in running parallel determinations serve as a check on the result of a single determination and thus increase our confidence in the reliability of the value obtained (assuming that good accordance is secured) and besides give an average value that is probably more nearly correct than a single value as far as accidental errors are concerned.

The values obtained in parallel determinations should agree reasonably well among themselves. In most analyses in which the percentage of the constituent present is not too small (major constituents), the differences should usually not be greater than three parts per thousand. Obviously, if the results of duplicate or triplicate determinations show considerable differences, not much confidence can be placed on any one result; and it is then necessary to run extra determinations until satisfactory concordance is obtained. The running of duplicates is of special value in detecting mistakes and blunders. If two or more results agree excellently, it is by no means justifiable to conclude that the value obtained is correct. Students often entertain this erroneous notion. Good concordance merely indicates that the accidental errors, or variations in the determinate errors, of all the determinations is the same or nearly the same. There may still be a very large constant error associated with the result (cf. Fig. 67). Good agreement in parallel determinations signifies that the determinations have been made under closely similar conditions; it does not guarantee the accuracy of the results. Failure to obtain satisfactory agreement in parallel determinations is, however, evidence that operative errors or mistakes have been made.

We have already seen (p. 275) that the larger the number of measurements, the smaller the deviation of the mean is likely to be from the true value, as far as the indeterminate class of errors is concerned. The number of parallel determinations that should be run in an analysis depends to a great extent upon the importance attached to the result. In an atomic-weight determination, for example, eight or ten or even a greater number of determinations are made. Similarly, in establishing the accuracy of a method or the suitability of a standard substance (p. 440), a large number of parallels is run. In ordinary analysis duplicate or triplicate determinations usually suffice. In most cases duplicate analyses are preferred to triplicate, because the slightly greater reliability of result obtained by the latter is more than counterbalanced by the longer time and the greater supply of apparatus then required. The analyst should aim to work so carefully that the difference obtained in duplicate determinations will be so small that a third determination cannot appreciably affect that difference. For the beginning student, however, it may be advisable to run the first one or two analyses in triplicate. Analyses should be run at least in duplicate unless a complete analysis is being made, in which case the results can be checked by summation, as described later.

In standardizing a volumetric solution, it is desirable to make three parallel determinations because the error in the titer of such a solution must be as small as it is practicable to make it, since an error in the standardization is transmitted and added to the error made in the determination itself.

Summation. When all the constituents of a sample have been determined directly, a check on the general accuracy of the whole analysis can be obtained by adding up the percentages of all constituents. The summation of a perfect analysis will of course be 100 per cent.[1] Because of unavoidable errors, this theoretical figure is never obtained. The summation may yield a figure either higher or lower than 100 per cent, depending upon the direction of the errors involved. A good analysis will give a summation that is very close to 100 per cent. The permissible difference cannot be exactly stated, since the difference will depend upon such factors as the kind and the number of constituents in the sample. Some analyses are naturally more difficult to make than others. A rock analysis in which twenty or so constituents are determined may be considered satisfactory when the summation gives a value lying between 99.75 and 100.50 per cent. In a simpler analysis a better summation would be demanded. An analysis summing up to slightly more than 100 per cent is generally considered more satisfactory than one giving a sum slightly less than the theoretical figure, because small quantities of foreign materials are introduced from the reagents and the utensils. A summation decidedly less than 100 per cent points to the omission of one or more constituents in the analysis.

A nearly perfect summation may be due, of course, to compensation of relatively large errors, but usually such a summation may be taken as evidence of the substantial accuracy of the analysis.

The ionic balance. In inorganic analysis we often deal with samples composed of electrolytes. The latter are built up of cations and anions, which naturally must be present in equivalent amounts in order that electroneutrality may be preserved. This fact may be applied in testing the accuracy of analyses of electrolyte mixtures, either solids or solutions. It is evident that the sum of all the cations, expressed in equivalents or milliequivalents, is equal to the sum of the anions in an ideally perfect analysis. As an example of the application of the principle of the *ionic balance*, take the following illustration:

A solution containing calcium, magnesium, sodium, potassium, chloride, sulfate, and bicarbonate ions was found to have the following composition:

	G. PER 100 ML.
Ca^{++}	0.4080
Mg^{++}	0.1339
Na^+	0.2070
K^+	0.0586
Cl^-	0.3763
$SO_4^=$	0.9990
HCO_3^-	0.6322

---

[1] Provided the atomic weights of the elements involved are accurately known, as they are for the common elements.

The ionic balance is tested by adding up separately the milliequivalents of cations and anions, respectively:

CATIONS	MILLIEQUIVALENTS PER LITER	ANIONS	MILLIEQUIVALENTS PER LITER
Ca^{++}	203.6	Cl^-	106.1
Mg^{++}	110.1	$SO_4^=$	208.0
Na^+	90.0	HCO_3^-	103.6
K^+	15.0		
	418.7		417.7

It will be seen that the agreement is satisfactory, since the difference is only 1 part in approximately 400, or 0.25 per cent. The analysis can therefore be considered reliable. On the other hand, if the respective figures 420 and 412 had been obtained, the analysis could not be regarded as satisfactory, for this difference is equivalent to 2.0 per cent, which is too large. An error in the determination of one or more constituents, or the presence of other ions, would then be indicated.

Independent methods of analysis. Sometimes it is possible to establish the accuracy of a result by making the analysis in an entirely different way. For example, iron may first be determined gravimetrically by precipitation as ferric hydroxide after removal of interfering elements, followed by ignition of the precipitate to ferric oxide. Then it may be determined volumetrically by reduction to the ferrous condition, followed by titration with a standard solution of an oxidizing agent such as potassium dichromate. If the results of two such radically different procedures give substantially the same result, it is highly probable that the values obtained are correct within small limits of error, because the same methodic errors, and even the same operative errors, can hardly be associated with both methods. This is a very good way of verifying a result and should be used whenever possible when much importance is attached to the result.

Methods of increasing the accuracy of analyses.

Such self-evident means of reducing the errors of chemical analyses as calibration of weights and volumetric glassware, purification of reagents when necessary, use of resistant vessels, and adherence to the proper quantitative technique need only be mentioned. It is also evident that a sample of suitable size must be taken, i.e., the sample must be sufficiently large to permit it and the precipitate which it yields to be weighed without unduly large percentage errors. Without attention to these mechanical details, no accuracy at all can be expected. In the following we shall consider chiefly the methods of minimizing the methodic errors, for these are the most serious and least easy to eliminate or reduce. Reduction of accidental errors by running parallel determinations has already been mentioned (p. 284).

1. *Application of corrections.* In many cases in which it is impossible to eliminate an error, it is possible to apply a correction for the effect it produces. Thus an impurity in a weighed precipitate may be determined and its weight deducted. The amount of a substance which remains unprecipitated may often be determined, and a correction thus found for solubility loss. The loss in weight which a platinum crucible undergoes on strong ignition may be determined by careful cleaning and reweighing. In many instances the labor involved in finding the correction values is so great that it is not worth while to make the corrections in ordinary analyses. Instrumental corrections (weights and buret especially) are often easily obtained and applied, however.

2. *Running of blank determinations.* Errors arising from the introduction of impurities through the reagents and vessels, and sometimes from other sources, can be allowed for by running what is called a blank determination. In making a blank, the sample is omitted; otherwise the details of the procedure are followed exactly as far as possible. The same amount of reagent is added, the same volume of solution is employed, the same temperature is used in the operations, the same period of time is allowed for each step, and so on. The precipitate finally obtained is weighed, if the determination is a gravimetric one, and the amount found is deducted from the weight of precipitate given by the sample. The blank is best carried along simultaneously with the sample. Although the errors arising from the sources mentioned above are often greatly reduced by running a careful blank, they are not always entirely eliminated or even minimized, because the conditions in the determination itself cannot be exactly reproduced in the blank. For example, the large amount of precipitate formed in the precipitation proper may carry down much larger quantities of a foreign substance than the small precipitate of the blank will do. If no precipitate is formed in the blank, as may happen when the reagents are very pure, the loss of precipitate resulting from its solubility is not included. It may be said that in general a small blank correction is better than none at all. A large blank correction is undesirable, because the exact value of the correction then becomes uncertain; in such a case purer reagents should be procured, or whatever other steps are necessary should be taken to reduce the blank.

It should be understood that the necessity for running a blank is not the same in every determination. In some determinations a blank can safely be omitted, while in others it is unconditionally necessary. For example, a gravimetric chloride determination with silver nitrate as reagent hardly requires a blank determination if the distilled water and nitric acid used are tested for chloride and found to be free of the ion. On the other hand, a determination of sulfur in a steel by the gravimetric method in which the element is finally weighed as barium sulfate would give entirely erroneous results unless the correction value obtained in the blank be applied. In this case small amounts of sulfur derived from the reagents and the gases of the flame will cause a large error in the result, because of the small percentage of sulfur in the sample.

3. *Control determinations.* It is possible to check the result of an analysis, or correct the value obtained, by taking a known amount of the constituent in question and performing the analysis involving it in the same manner as the analysis of the unknown. Since the amount of the constituent that should be found is known, the error of the *control* is obtained directly; and this correction can then be applied to the result found in the analysis of the unknown, provided certain conditions are fulfilled as discussed below.

The amount of constituent taken for the control analysis should be approximately the same as the amount present in the unknown, because the errors involved may be a function of the concentration or quantity of the constituent present. The proper amount of the constituent in question is obtained by weighing out a pure substance containing a known percentage of the constituent to correspond to the quantity found in the analysis of the unknown. A difficulty is introduced by the presence of foreign substances accompanying the desired constituent in the unknown sample. The control solution should, of course, include all the various substances present in the unknown, and, moreover, in the same amounts. The chief errors of a method may have their origin in the foreign constituents present; these substances may coprecipitate, or even precipitate, with the constituent in question, they may increase the solubility of the precipitate, and otherwise interfere. It will be seen then that a reliable control determination may require a complete preliminary analysis of the unknown. When the composition of the unknown has been determined, it is a simple matter to make up a synthetic mixture approximating the composition of the sample and to analyze the solution in exactly the same manner that the unknown was first analyzed. The method of controls is a very effective one for detecting methodic errors and determining their magnitude.

The difficulty introduced by the incomplete knowledge of the composition of the unknown can be overcome in a less satisfactory manner by adding a known amount of the constituent sought to a known amount of the unknown (already analyzed for the constituent) and comparing the result obtained with the result that should be obtained. Although this method is often capable of giving excellent service, it should be used with caution, because evidently the conditions of the control analysis are not exactly those of the determination itself (for example, the error due to solubility is not eliminated).

The known amount of constituent required for the control determination is obtained, as already indicated, by weighing out a pure substance (very often a salt) of known composition, containing the constituent as such or capable of furnishing it on proper treatment. It is of prime importance that the substance used be pure, or that it contain so little impurity that it will not affect the results. Generally an easily soluble substance is taken which can be purified by recrystallization or by some other method as discussed in Chapter XI. The purity of the substance cannot be accurately established by determining the main constituents. It is necessary to apply qualitative tests of known sensitivity and thus set an upper limit to the amount of foreign substances present. In some cases it may be necessary to determine the small amounts of the impurities present and deduct the quantities found to give the percentages of the main constituents. The presence of foreign water must especially be guarded against. In normally anhydrous substances it can be detected and determined by the methods described in Chapter XVI. Hydrated substances are less reliable than anhydrous ones as standards, because it is not always an easy matter to determine whether the theoretical amount of water is actually present.

It will be seen that checking or increasing the accuracy of analyses by the method of controls involves considerable time and labor, and therefore it is not often applied to a *determination*. It is, however, frequently used in investigating the accuracy of a *method* and, indeed, is then of fundamental importance.

Standard samples. Related to the method of controls is the use of standard samples. In the case of the more or less complex natural materials or artificial products, it is found advantageous to prepare a sample of the material in question and to analyze it carefully by reliable methods, preferably by having a number of skilled analysts make the analysis independently. The averages of the results obtained in the most careful analyses by the coöperating analysts are taken as the most probable values. A sample thus analyzed is known as a standard sample. Standard samples serve the purpose of revealing operative and personal errors, as well as some methodic errors, made either in the analysis of the sample itself or of a sample having a similar composition. Standard samples are further very useful in the investigation of the accuracy of a new method. Moreover, they may be used for standardizations (cf. p. 440).

The United States Bureau of Standards prepares, analyzes, and sells standard samples of irons, steels, ores, etc., as well as certain primary standards (sodium oxalate, benzoic acid, potassium acid phthalate, arsenious oxide).

Empirically determined correction values from control determinations. By taking various known amounts of a constituent and making the analysis according to a fixed procedure, it is possible to set up a table of correction values that can be applied in the analysis of an unknown sample. One looks up in the table the correction corresponding to the weight of precipitate obtained in the analysis of the unknown and adds it algebraically to obtain the corrected weight. Winkler[1] has given tables of such correction values for calcium, magnesium, sulfate, and many other constituents. Naturally when use is made of such empirically determined corrections, great care must be taken to make the analysis in exactly the same way as directed in the procedure, for otherwise the corrections do not apply. The chief objection to such corrections is that the presence of foreign substances may alter the values entirely. Nevertheless, corrections of this kind have a certain value in practical analysis. They are most valuable when numerous analyses of samples of the same nature are being made. The analyst should in such a case construct his own table of corrections and ascertain what effect the variation in amount of the other constituents of the sample has upon the correction values.

4. *Varying the conditions of analysis.* A *method* of analysis can often be improved by varying the conditions in a systematic manner. In an analysis involving the formation of a precipitate, the most important variables are:

1. The chemical composition of the solution in which the precipitate is formed.
2. The concentration of the solution.
3. The temperature of precipitation.
4. The manner of precipitation: speed of addition of reagent, manner of mixing (reagent to solution or vice versa).
5. Treatment after precipitation: time of standing, digestion, wash solution used, etc.

The first factor, the composition of the solution, is a most important one. Constituents which would be precipitated with the substance sought must necessarily be removed or otherwise rendered incapable of precipitation or interference. Generally, if such interference is possible, a *separation* of the interfering substances from the constituent in question must be made. The separation is usually made either by precipitating the undesired constituents or by precipitating the constituent sought. In either case a reprecipitation is usually required. Sometimes physical and semiphysical methods of separation are applied. The accurate determination of a substance in a pure solution is nearly always an easy matter. The determination of the same substance when it is associated with others may be, and often is, one of great difficulty, as we have already emphasized. Methods of separation are often imperfect, and there is room for much improvement in this field.

Even when the foreign substances present do not yield precipitates with the reagent added, it is often found that the precipitate of the desired constituent contains greater or lesser amounts of the former. This phenomenon has been given the name *coprecipitation* (Chapter VIII). It is a most troublesome source of error in analyses involving precipitations. It is never possible to predict with certainty whether a given precipitate can be obtained sufficiently pure for quantitative purposes if other substances, normally unprecipitable, are present. Great caution must therefore be used in applying to a mixture a method which works well for a pure substance, even if the other substances do not precipitate of themselves with the reagent used. Thus sulfur in a sulfate solution cannot be determined with any accuracy by precipitation as barium sulfate if chlorate or nitrate is simultaneously present. In spite of the easy solubility of barium chlorate and nitrate under the conditions of the determination, it is found that relatively large amounts of these salts are present in the barium sulfate precipitate. Good results can be obtained in this case only by destroying the chlorate and nitrate before precipitating the sulfate with barium.

---

[1] See L. W. Winkler, *Ausgewählte Untersuchungsverfahren für das chemische Laboratorium*, pp. 101, 104, 106, etc. (Vol. XXIX of the Margosches' series, Die chemische Analyse), Verlag Ferdinand Enke, Stuttgart, 1931. See also Winkler's papers in Z. angew. Chem.

In some instances foreign substances increase the solubility of a precipitate and may entirely prevent its formation as the result of chemical interaction (cf. the effect of large amounts of magnesium on the precipitation of calcium oxalate, p. 356).

Sometimes the interference of foreign substances can be prevented in a simple manner by a slight alteration in the conditions of the determination. Thus, by changing the acidity of the solution or by adding a complex-forming reagent, the precipitation of a foreign substance can often be avoided. Numerous instances of this kind will be mentioned in the subsequent chapters of this book.

Concerning the effect of the temperature of precipitation and the concentration of the solution at the time of precipitation, it is not necessary to say much at this point. These factors are considered in detail elsewhere. Variations in these conditions lead chiefly to a change in the amount of coprecipitated substance and in the filterability of the precipitate and are therefore of great importance.

It is possible to improve a method of analysis empirically by varying in turn the factors enumerated at the beginning of this section, while maintaining the others constant, and noting the effect of such changes upon the results. Or from theoretical considerations it may be possible to decide immediately what conditions should be changed to attain the desired results. The last is becoming more and more the method of modern analytical chemistry. It is one of the purposes of this book to indicate how the accuracy of analytical methods can be increased by the intelligent application of physico-chemical principles.

5. ***Resort to other methods.*** If a given method of analysis is unsatisfactory, either because it gives results of insufficient accuracy or otherwise, it is sometimes possible to reject it in favor of another one. An example of such a procedure is afforded by the methods of determining aluminum. The old procedure, which is the one still most extensively used, involves the precipitation of hydrous aluminum oxide with ammonium hydroxide and the ignition of the precipitate to aluminum oxide. In the new procedure the metal is precipitated as aluminum hydroxyquinolate by the organic reagent 8-hydroxyquinoline; the precipitate is dried at 130° and weighed as the hydroxyquinolate. Why is the newer method better than the old one in the point of accuracy? In the first place it is necessary to ignite aluminum oxide at a very high temperature to render it anhydrous, and the ignited residue is likely to be hygroscopic; aluminum hydroxyquinolate, on the other hand, is easily rendered anhydrous at a low temperature, and the dried precipitate is not hygroscopic. Secondly, the high molecular weight of the organic weighing form reduces the weighing error to negligible proportions and enables even very small amounts of aluminum to be determined with accuracy:

$$\frac{2\,\text{Al}}{\text{Al}_2\text{O}_3} = 0.5291, \frac{\text{Al}}{\text{Al(C}_9\text{H}_6\text{ON)}_3} = 0.05872.$$

It should not be forgotten that a radical change in procedure may enable determinations to be made with accuracy that could otherwise not be made at all. Where gravimetric and volumetric methods fail, a colorimetric method may, for example, give the desired results.

Accuracy in indirect analysis.

If a given mixture consists of two constituents, the respective amounts of each may be found by a so-called *indirect analysis* (see p. 30). Such a method never yields highly accurate results and should never be applied to the determination of a constituent which is present in very small quantities. The indirect method is sometimes applied in testing the purity of a salt. However, the result of such an analysis will not give a guarantee that the salt tested is pure. This will be clear from the following example.

Suppose that a mixture consisting of potassium chloride and sodium chloride is analyzed indirectly. The sum of the two constituents is found by weighing the anhydrous chlorides, and a weight, say, of 0.3000 g. is obtained. The chloride content of this weighed sample is then determined by precipitation as silver chloride. If the sample were pure potassium chloride, 0.5768 g. of silver chloride would be found; if pure sodium chloride, 0.7357 g. The difference between these two weights amounts to 0.1589 g. Each 1.589 mg. difference between 0.7357 g. and the weight found corresponds to 1 per cent potassium chloride in the sodium chloride. Suppose now that the sum of the errors in the weighing of the mixed chlorides and the determination of silver chloride amounts to 0.5 mg.; this error would correspond to an absolute error of 0.31 per cent potassium chloride in the mixture. If the latter should contain only 1 per cent of potassium chloride, the relative error in the determination of this constituent would amount to 31 per cent. If the mixture contained 10 per cent of potassium chloride, the relative error would be 3.1 per cent; if it contained 50 per cent, the relative error would be 0.62 per cent.

It is seen that the absolute error decreases with increasing difference between the conversion factors of the two components. In the above example, it would have been possible to transform the two chlorides into the perchlorates and to determine the weights of the mixed chlorides and mixed perchlorates. 0.3000 g. of pure potassium chloride would yield 0.5575 g. potassium perchlorate; 0.3000 g. of pure sodium chloride would give 0.6282 g. sodium perchlorate. The difference in weight corresponds to 0.0707 g. Assuming again the sum of all errors to be 0.5 mg., we find that this corresponds to an absolute error of 0.71 per cent potassium chloride. If the salt mixture contained 1 per cent potassium chloride, the relative error would amount to 71 per cent; if it contained 10 per cent of potassium chloride, to 7.1 per cent, etc.

In an indirect analysis it is also possible to make a combination of the weight of a certain mixture and the result of the volumetric determination of one of its constituents. Suppose, for example, that the weight of a mixture of potassium chloride and potassium bromide is 0.3000 g. The sum of chloride and bromide is determined by titration with 0.1000 N silver nitrate according to the method of Mohr (see p. 471). 0.3000 g. of pure potassium chloride requires 40.24 ml. 0.1 N silver nitrate, and 0.3000 g. of pure potassium bromide requires 25.21 ml. The difference between these two figures is 15.03 ml. of 0.1000 N silver nitrate. Suppose now that the sum of the errors in the volumetric determination amounts to 0.05 ml. of silver nitrate. This error is equivalent to an absolute error of $\frac{0.05}{0.15} = 0.33$ per cent of potassium bromide in the mixture. If the latter contained 1 per cent potassium bromide, this error would correspond to a relative error of 33 per cent; if it contained 10 per cent, to 3.3 per cent, etc. Therefore, it is not possible to find a small amount of potassium bromide in potassium chloride by this indirect method with any reasonable degree of accuracy. A constituent occurring in small amounts must be determined by a direct method.

Accuracy in calculations.

At this point it may be well to consider briefly the matter of accuracy in the calculation of results. Naturally, care must be taken not to decrease the accuracy of the value reported in an analysis by unwarranted approximations in computations. On the other hand, the final value of an analysis should be expressed in such a way that the accuracy of the result is indicated, i.e., the number of figures in the reported result should be consistent with the probable precision of the analysis.

Significant figures. As the name implies, significant figures of a number are those that have some practical meaning. The number of significant figures in an experimentally determined value expresses the precision with which the measurement has been made. *The significant figures of a number include all the certain digits and the first* (*and first only*) *doubtful digit of that number.* Thus, if an object has been weighed to the nearest 0.1 mg. on the analytical balance, its weight is recorded correctly by stating the value in grams to the fourth decimal place, e.g., 12.1230 g. There are six significant figures in this number. It would be incorrect in this case to give the weight as 12.123 g., for this would imply that the weighing was made only to the nearest milligram and that the probable precision is ± 1 mg. On the other hand, if the object were weighed on a rough balance sensitive to 0.01 g., it would be incorrect to record the value as 12.120 g.; the weight should then be put down as 12.12 g. Particular attention should be paid to the final zeros of numbers. They must never be omitted when they are significant figures nor included when they are not significant. Students seem apt to err in this regard.

When the zero comes before the decimal point and no decimals are given, it is impossible, of course, to tell whether it is a significant figure. For example, the value of the faraday is given as 96,500 coulombs. One cannot know whether the zeros are significant, because if this number contained only three significant figures it would still be necessary to insert the zeros to place the decimal point. Actually the first zero in 96,500 is a significant figure and the second is not, since the measured value lies with great probability between 96,490 and 96,510. The precision can be indicated by writing the value as 96,500 ± 10 or as 9.650×10^4.

Zeros lying immediately after the decimal point are not significant figures. Thus, in the number 0.0019 there are only two significant figures.

Hurley[1] has made the following suggestion regarding the writing of the last significant figure:

> "Perhaps the most satisfactory way to treat the last significant figure is to give a rough indication of its doubtfulness by the use of subscripts. Using this convention, a measurement written as 21.23 would indicate a precision (average deviation of a single observation) of ± 0.01 unit. If the average deviation is greater than this, the number would be written as 21.2_3. The adoption of this convention reduces all rules for the use of significant figures to the following. In writing a number which represents a measured quantity, use the number of significant figures which comes nearest to expressing the real precision of the measurement, using a subscript if the last figure is less precise than ± 1."

Computations. In carrying through a series of computations, it is best to retain one digit beyond the last significant figure in order that the latter may not be altered in the arithmetical processes. Thus, in obtaining the average of 25.05, 25.07, and 25.07, the result should be written 25.063 if this number is to be used in calculations; otherwise the last significant figure alone is retained: 25.06. In rounding off values to the significant figure, the succeeding digit is dropped if it is less than 5; if it is 5 or greater, the significant figure is increased by 1. Thus the average of 0.1246, 0.1244, and 0.1247 is 0.1246 (0.12456).

---

[1] F. H. Hurley, J. Chem. Educ. *17*, 334 (1940).

In multiplications and divisions it must be remembered tnat it is the percentage of uncertainty, and not the absolute uncertainty, that is transmitted to the result. Thus $(10.01 \pm 0.01) \times (10.01 \pm 0.01) = (100.2 \pm 0.2)$. Therefore the product 5×23.41 should be written 117.1; or if the value is to be used in further computations, one more figure is retained: 117.05. The use of logarithms is very advantageous when a number of multiplications and divisions are to be made. Not only is the time required for the computations much less than in the long-hand method, but the superfluous figures obtained in ordinary multiplication are automatically dropped and the last figure rounded off. Four-place logarithm tables are sufficiently precise for most analytical calculations, but it is convenient to use five-place tables to avoid interpolating. A slide rule may be used for checking results to detect errors in computation of the order of a tenth of a per cent, but it should not be used in the first place to obtain the results, since it usually is not capable of giving sufficiently exact results.

Statement of final results. It should be realized that the result of a calculation involving several experimentally determined quantities can be no more accurate than the least accurate value included. As an illustration of this point let us take a case in which a sample is analyzed for sodium by precipitating the element as sodium zinc uranyl acetate and weighing as such. Suppose that the weight of sample taken was 0.0496 g. and that the weight of precipitate obtained was 1.0220 g. The percentage of sodium present then is:

$$\frac{1.0220 \times \dfrac{\mathrm{Na}}{\mathrm{NaC_2H_3O_2 \cdot Zn(C_2H_3O_2)_2 \cdot 3\,UO_2(C_2H_3O_2)_2 \cdot 6\,H_2O}}}{0.0496} \times 100$$

$$= \frac{1.0220 \times 0.01495 \times 100}{0.0496} = 30.8.$$

Note that the result is reported as 30.8 per cent, and not as 30.80 or 30.802. There are several good reasons for this. First, it should be noted that since the error in weighing the sample may amount to about 0.2 mg. the result may be in error to the extent of 1 part in 250 $\left(\text{i.e., } \dfrac{2}{496}\right)$ from this source alone. The error in weighing the dried precipitate is only 1 part in 5000, but this high precision cannot be taken into consideration when determining the number of figures to be used in the final result, since it is more than cancelled by the error in weighing the sample. Then the probable accuracy of the *method* must be taken into account. The method probably is accurate to 1 part in 500 in the hands of a practised analyst. Taking these facts into consideration, it is apparent that the percentage should be reported as 30.8, because the accuracy of this particular determination is not likely to be greater than 1 part in 300. The figure following the decimal point is the first doubtful digit. It would be incorrect to write the result as 30.80, because this would imply that the value is correct to the figure in the first decimal place; and this is not true. Incidentally, it is a waste of time to weigh the dried precipitate to the nearest 0.1 mg.; weighing to 1 mg. is sufficiently precise because such weighing introduces an error of 1 part in 500 at the most.

In ordinary analysis it is seldom that a result can be relied on to ± 0.1 per cent (relative error), so that more than four significant figures should never be used in reporting a result. In some cases three significant figures will suffice. The agreement between duplicates should be taken into consideration when deciding how many figures to include in the average. If the results of a duplicate analysis give, say, the percentages 62.04 and 62.39, it would be useless and absurd to state the average as 62.22, because even the third figure is uncertain; the mean should be written simply 62.2 per cent. On the contrary, if the duplicates gave the values 62.03 and 62.09 per cent, it is correct to write the mean as 62.06 per cent, because when so written the figures indicate that the result is correct to the first decimal place but not to the second. In no case should there be more than one uncertain figure in the result stated.

PROBLEMS

1. Classify the following errors as additive or proportional (or as both or neither): impurities in reagents, solubility of a precipitate, adsorption of moisture by an ignited residue and by a weighing vessel, electrification of object weighed, coprecipitation, volatilization of a constituent during decomposition of the sample, use of uncalibrated weights, use of wrong chemical factor, personal equation, buoyancy of air in weighing, balance arms of unequal length.

2. A determination of bromine in pure potassium bromide yielded the percentage 67.03. What is the absolute and relative error of the result?

Ans. Absolute error = − 0.12 per cent; relative error = − 0.18 per cent or − 1.8 parts per thousand.

3. In a study of the suitability of a certain method for the determination of sodium, the following results were obtained:

NaCl Taken g.	NaCl Found g.
0.01263	0.01257
0.01127	0.01128
0.01215	0.01207
0.01185	0.01186
0.01317	0.01312
0.01258	0.01252

(a) Find the average error of the determinations.

(b) May it be concluded that a constant error exists?

4. A standardization of a solution of hydrochloric acid against sodium carbonate with the use of a weight buret gave these values for the normality of the acid:

0.18079
0.18087
0.18087
0.18091
0.18083
0.18085
0.18083

Find the average, standard, and probable deviations of a single titration. Also calculate the standard and probable deviations from the average deviation. Should any of the results be rejected?

Ans. Average deviation = 0.000029, standard deviation = 0.000035 (0.000036 calculated from average deviation), probable deviation = 0.000025 (0.000025 calculated from average deviation); no result should be rejected.

5. The acid of Problem 4 was also standardized against borax and sodium bicarbonate, the following values for the normality being found:

Borax	$NaHCO_3$
0.18081	0.18064
0.18080	0.18067
0.18081	
0.18085	
0.18085	

(a) Are the borax and the sodium carbonate of Problem 4 of the same purity within the experimental error of the titrations?

(b) If it is assumed that the sodium carbonate is entirely pure, what conclusions can be drawn about the purity of the sodium bicarbonate?

(c) What conclusions can be drawn regarding the *accuracy* of the normality of the hydrochloric acid on the basis of the titrations against sodium carbonate and borax?

Ans. (a) The mean normality of the acid and its probable deviation from titrations against sodium carbonate is 0.180850 ± 0.000009; the mean normality from titrations against borax is 0.180824 ± 0.000008. To determine whether the difference between the two means is statistically significant, divide the difference by the square root of the sum of the squares of the probable deviations: $\frac{0.180850 - 0.180824}{\sqrt{(9 \times 10^{-6})^2 + (8 \times 10^{-6})^2}} = ca.\ 2$. The probability corresponding to this ratio is slightly greater than 0.8 (Table XLIII).

This probability is not sufficiently great to indicate with reasonable certainty a difference in purity between the two standard substances.

6. Four parallel determinations of a constituent gave the values 20.20, 20.17, 20.23, and 20.14 per cent. What is the probability that the indeterminate error of the average does not exceed 2 parts per thousand?

7. (a) If the average deviation of single weighing is 0.1 mg., what weight of sample should be taken in the gravimetric determination of chlorine as silver chloride in a sample containing 30 per cent of chlorine, in order that in the long run the average deviation of the result shall be 1 part per thousand?

(b) What weight of sample should be taken in order to make it practically certain that this deviation shall not be exceeded as a consequence of weighing errors?

Ans. (a) 0.18 g.; (b) 0.7 g.

8. Show that if P = percentage of constituent
N = normality of standard solution
E = equivalent weight of constituent in titration
w = average deviation of a single weighing in grams
v = average deviation of buret reading in ml.,

the weight of sample S that must be taken in a volumetric determination to yield an average deviation $\pm\, p_r$ in parts per thousand in the percentage of the constituent found is

$$S = \frac{140}{p_r}\sqrt{100\,w^2 + \left(\frac{NEv}{P}\right)^2}.$$

(a) What weight of sample must be taken to make the average deviation of the percentage of the constituent equal to 1 part per thousand in a titration with 0.1 N solution if the percentage of constituent is 100, its equivalent weight is 50, and a weighing can be made to ± 0.1 mg. on the average, and the buret can be read to ± 0.01 ml.?

(b) What weight of sample should be taken to make it virtually certain that the average deviation of 1 part per thousand shall not be exceeded?

(c) Will more than 50 ml. of standard solution be required for the titration of the sample of (b)? *Ans.* (a) 0.15 g.; (b) 0.6 g.

9. (a) Five determinations of ZrO_2 in a clay yielded the percentages 0.21, 0.23, 0.24, 0.22, and 0.23. How shall the average be reported? Why?

(b) In a determination of water in a sample of $CaSO_4 \cdot \frac{1}{2}\,H_2O$, 0.2402 g. of the material was ignited to expel the water and the loss in weight found. If the weighings were made to ± 0.1 mg., how many figures shall be used in expressing the percentage? *Ans.* (a) 0.23 per cent.

GRAVIMETRIC DETERMINATIONS

CHAPTER XVI

DETERMINATION OF WATER

A discussion has already been given (Chapter IX, p. 136 *et seq.*) of the forms in which water can exist in solids. The determination of water in solids is a matter of considerable importance. Not infrequently water is an essential constituent of a substance. Nonessential water, such as water of hygroscopicity, affects the percentages of other constituents as found by analysis; and for this reason, if for no other, it must be taken into consideration (cf. p. 241). The water content of a substance must always be determined when a complete analysis is made.

In contrast to the determination of other constituents, that of water is based, usually, on its physical behavior. According to circumstances water can be determined directly or indirectly.

Indirect method for the determination of water.

In many cases, water can be determined indirectly from the loss in weight the sample undergoes when the water it contains is expelled by heating or exposure to a dry atmosphere (as in a desiccator). Obviously, this method can be applied only when (1) water is the only constituent volatilized, and (2) the residue does not change in weight as the result of oxidation, hydrolysis, etc.

Hygroscopic water or *moisture* is commonly determined from the loss in weight shown by a sample after heating to constant weight at some more or less arbitrary temperature, usually 105° as we have already explained (p. 241). It should be borne in mind that essential water can also be lost at the same temperature in such samples as hydrated salts for instance, whereas, on the other hand, in finely divided material all of the nonessential water may not be removed at 105°.

The indirect method can also be applied to the determination of essential or total (*essential* + *nonessential*) water in substances which give physically and chemically stable residues at the temperature required for the complete expulsion of the water. Examples of substances falling in this class are gypsum ($CaSO_4 \cdot 2\ H_2O$), barium chloride dihydrate, calcium hydroxide, etc. The temperature to which a substance must be heated to render it water-free depends, of course, upon the nature of the substance. Many hydrated salts readily lose their water at 105°, although some are stable at the same temperature. Water chemically held as hydroxide requires a high temperature for complete removal. Aluminum hydroxide, for example, retains traces of water tenaciously even at the temperature of the blast lamp. The dehydrated products obtained in the indirect water determination are often very hygroscopic, and due care must be taken in weighing them.

Substances such as organic compounds, which decompose at relatively low temperatures, may sometimes be deprived of their water by heating at as low a temperature as possible *in vacuo* (use of a vacuum drying oven), or by exposure to the dry atmosphere of a desiccator charged with a vigorous dehydrating agent such as sulfuric acid, magnesium perchlorate, or phosphorus pentoxide, or, better, by passing desiccated air over the sample. By resorting to such procedures, it may also be possible to determine both the essential and nonessential water content of such substances.

It may be mentioned that it is sometimes possible to determine water indirectly in substances that would otherwise decompose, by adding a suitable flux. For example, aluminum sulfate cannot be completely dehydrated without expelling sulfur trioxide. If, however, the sulfate is mixed with previously ignited sodium paratungstate ($5\ Na_2O \cdot 12\ WO_3$), the water can be completely expelled by heating the mixture to a high temperature, since the flux retains the sulfur trioxide, forming stable sodium sulfate, and the loss in weight is due only to the water lost.[1]

Determination of water of hydration of barium chloride dihydrate. As an example of the indirect method, the determination of the water of hydration of barium chloride dihydrate may be taken as typical. The aqueous tension of barium chloride dihydrate at 20° is 1.3 mm. of mercury, and at 35° it is 11.6 mm.; the hydrate is therefore stable in the atmosphere except under conditions of unusually low humidity. The salt readily loses all its water of crystallization at temperatures above 100°, but much higher temperatures can be used in the dehydration since anhydrous barium chloride is stable and nonvolatile at even fairly elevated temperatures. The dihydrate shows little tendency to occlude water in vacuoles, so that the loss in weight represents very closely the water of hydration. Since the salt is weighed out in the form of coarse crystals, the amount of adsorbed water associated with it is negligibly small.

---

[1] S. B. Kuzirian, Am. J. Sci. [4] *36*, 401 (1913); Z. anorg. Chem. *85*, 127 (1914).

Procedure. Coarsely powder C. P. or analytical grade barium chloride dihydrate in a mortar, and weigh out 1 g. duplicate samples, proceeding as follows. Dry a 15 ml. glass-stoppered weighing bottle in an oven at 105°, cool in a desiccator, and obtain the weight of the empty stoppered bottle to 0.1 mg. Transfer the approximate weight of the sample to the bottle with the aid of a spatula, and reweigh to 0.1 mg. Then place the weighing bottle and its contents in an oven heated to 105° or higher. Lay the stopper on its side over the mouth of the bottle to permit the free escape of water vapor.[1] Heat for 1 hour at 105° (or ½ hour at 150° to 200°), then stopper the weighing bottle, and place it in a desiccator to cool to room temperature (p. 223). Before weighing, loosen the stopper to equalize the pressure. Keep the bottle stoppered during the weighing. Unstopper the bottle after weighing, return it to the oven, and heat as before for ½ to 1 hour. Cool, weigh, and repeat the heating if necessary until the weight is constant to 0.2 mg. Then calculate the percentage of water in the sample from the loss in weight found. Each sample should give a result agreeing within 0.05 absolute per cent with the calculated value, $\frac{2\ H_2O \times 100}{BaCl_2 \cdot 2\ H_2O} = 14.75$ per cent.

Direct method for the determination of water.

If the sample volatilizes or decomposes on heating to the temperature required to expel water quantitatively, the indirect method for water can naturally not be used, and the determination must be made by the direct method, in which the water evolved is absorbed in a suitable drying agent which is weighed before and after the absorption; the gain in weight of the absorbent then represents the weight of water present, provided that no other substance save water is taken up by the desiccant. It may be necessary to mix the sample with an anhydrous flux to retain volatile substances and to aid in the expulsion of water from substances not easily deprived of water on heating. Thus, in the determination of water in ferric sulfate by the direct method, sulfur trioxide as well as water is expelled on heating. Entirely erroneous results would be obtained if no provision were made for the retention of the sulfur trioxide, since the latter would otherwise be absorbed to a large extent in the drying agent and would count as water. The volatilization of sulfur trioxide can be prevented in this case by mixing the ferric sulfate with anhydrous sodium paratungstate, for example; the latter holds the sulfur trioxide, forming sodium sulfate, which is not decomposed unless the temperature be raised unnecessarily high.

---

[1] In cases where the sample decrepitates, the mouth of the vessel in which the heating is done should be covered loosely at first to prevent loss of flying particles. This need not be done in this case.

Alternatively, the vapors can be passed over a "retainer" before being led into the absorption tube. Thus lead oxide (a mixture of PbO and PbO_2 is generally used) heated above 250° fixes sulfur trioxide and dioxide by forming lead sulfate. This retainer is also useful for catching other acidic substances such as hydrogen chloride and is used frequently in organic elementary analysis. With the aid of lead oxide it is possible to determine water in hydrolyzable salts such as magnesium chloride. The hydrates of such salts hydrolyze to the oxide or a basic salt when heated to expel water, e.g.: $MgCl_2 \cdot H_2O \rightleftarrows MgO + 2\,HCl$. Some of the hydrogen which should be evolved as water is set free as hydrogen chloride instead. However, if the gases are passed over hot lead oxide, the hydrogen chloride forms lead chloride and gives the equivalent amount of water; and correct results are obtained:

$$PbO + 2\,HCl \rightarrow PbCl_2 + H_2O.$$

In these and similar cases the hydrolysis can be prevented by heating in a current of dry hydrogen chloride.

Apparatus. The set-up shown in Figure 70 is representative of assemblies used for the direct determination of water in solids.

The gas wash bottle *A* contains concentrated sulfuric acid and serves the double purpose of removing most of the water vapor from the entering air-stream and indicating the speed with which air is being drawn or forced through the train. *B*, which may be a drying tower or U-tube, is filled with magnesium perchlorate or other efficient dryer having an aqueous vapor pressure less than that of sulfuric acid. The tube *C* may be made of hard glass or Pyrex, porcelain, or fused silica, depending upon the temperature to which the sample must be heated. It may conveniently have a length of 40 to 50 cm. and a diameter of 1.5 cm. Preferably it should be tapered at the exit end so that it can be connected directly to the absorption train. The sample is heated in the porcelain or platinum boat *D*. *E* is a mixture of lead oxide and lead dioxide intermixed with glass wool, for example, and placed between plugs of the same material. This retainer need only be included when the sample gives off sulfur oxides, hydrogen chloride, or other acidic compounds. The tube *C* may be heated with burners or, better, electrically in a tube furnace. The temperature of

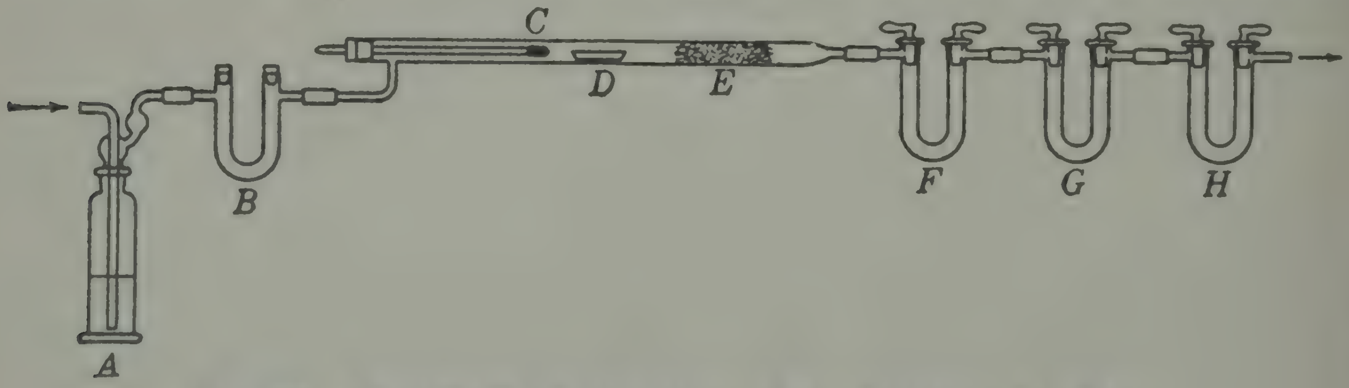


FIG. 70. Apparatus for the direct determination of water.

the hot zone of the tube corresponding to a given height and position of the burners, or to the setting of the rheostat of the electric furnace, should be determined prior to the determination by inserting a thermometer or thermocouple through the front end of the tube; or, better, either of these should be kept in place during the determination. The mass of lead oxides *E* should be maintained at a temperature of 300° to 350°.

The tube *C* is connected to the absorption train *F*, *G*, *H* by means of a thick piece of rubber tubing; the ends of the tubes of *C* and *F* should be in contact. As absorption vessels, U-tubes will serve.[1] Generally it is best to have two weighed absorption tubes (*F*, *G*) in the train. The absorbent in the last weighed vessel *G* should be the same as that in *B*, but that in *F* need not be so necessarily. Thus it may be advantageous to put the cheaper desiccant calcium chloride in the first absorber *F* and follow it with magnesium perchlorate in *G*. If carbon dioxide is evolved on heating the sample, calcium chloride should not be used in *F*, because this desiccant is likely to contain calcium hydroxide which will take up carbon dioxide; this impurity cannot be completely removed by pretreating with carbon dioxide (p. 384). These absorption tubes should be weighed against similar tubes used as tares. The last tube in the train, *H*, is simply a protecting tube for *G*; it should be filled with the same desiccant as *G*. *H* is connected to the vacuum line or an aspirator; as already mentioned, air can be forced instead of drawn through the system, the former method being perhaps preferable. Before use the assembly should be tested for air-tightness (cf. p. 387).

Determination of water of constitution of sodium bicarbonate.[2] As an example of the direct method for water, the determination of the elements of water in sodium bicarbonate may be taken. Sodium bicarbonate is quantitatively decomposed into sodium carbonate and water when heated to 270° to 300°:

$$2\ NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2.$$

Any hygroscopic or included water present is counted with the combined water when an air-dried sample is used.

Procedure. Set up a train similar to the one described in the previous section and depicted in Figure 70. Place concentrated sulfuric acid in *A* and anhydrous magnesium perchlorate or calcium sulfate (drierite) in *B*, *F*, *G*, and *H*. Omit *E*.

Heat the central part of the tube *C* with the empty boat *D* in place (Fig. 70) to approximately 300°; and with *F*, *G*, and *H* disconnected, draw or force air through *A*, *B*, and *C* for about 10 minutes at the rate of 2 or 3 bubbles per second. Then connect in *F*, *G*, and *H*, and continue to pass air through the hot tube for 10 minutes. At the end of this time stop the air current, close *F*, *G*, and *H*, and place *F* and *G* in or near the balance case. After 15 minutes open the tubes momentarily, and weigh separately against a similar tare. Replace the tubes in the train, open them, and again pass air through the system for 10 minutes. Then weigh

---

[1] If the sample contains much water, it is advantageous to employ for *F* a U-tube with a bulb on the entrance side to hold the water expelled, thus saving the desiccant.

[2] Malachite (basic copper carbonate) or white lead may also be used as samples.

F and *G* as before. If their weights are constant to 0.3 mg., proceed with the determination as described in the next paragraph; otherwise replace them in the system and continue as before until constant weight is obtained, showing that all moisture has been swept out of the apparatus.[1]

Weigh 0.5 g. of air-dried C. P. sodium bicarbonate into the cold boat, and replace the latter in the central part of the cold tube *C*. With *F*, *G*, and *H* in the train, start a current of air through the system at the rate of 2 or 3 bubbles per second, and then begin to heat the tube gently in the neighborhood of the boat. If any water condenses between *D* and the entrance end of the tube *C*, increase the rate of flow. Gradually increase the heat until the sample is at 300°, and maintain it at this temperature for 15 to 30 minutes. If there is any condensed water on the walls of *C* between the boat and the exit end, cause it to be carried over into *F* by brushing the tube carefully with a flame. Continue the passage of air through the train until the tube *C* is cold and no water droplets are visible anywhere in the tube. Then close and disconnect *F*, *G*, and *H*. Allow *F* and *G* to stand in the balance case for 15 minutes, and weigh as before against a tare. Replace the tubes in the train, and proceed as before until constant weight (0.3 mg.) is attained. From the gain in weight obtained in duplicate analyses, calculate the percentage of water in the sample, and compare with the theoretical value.

NOTE:

If desired, the carbon dioxide evolved can be determined at the same time as the water by inserting a tube filled with ascarite and desiccant (see p. 386) between *G* and *H* and finding its increase in weight. In this case a tube of ascarite must be included in the purification end of the train, between *A* and *B*, to remove carbon dioxide from the air stream. The loss in weight of the sample as determined from the weight of the residue should be equal, within the experimental error, to the sum of water and carbon dioxide found.

When so performed, the experiment simulates the determination of carbon and hydrogen in an organic compound by burning the latter and obtaining the weight of carbon dioxide and water formed.

Other direct methods for water.

A direct method for water, in which no absorption tube is used, is that of Brush-Penfield; it is suitable for the determination of water in solids which contain the constituent in small amounts and give it off at not too high temperatures. The method is described on p. 753.

When determining water in organic compounds, one is often confronted with the difficulty that the sample is more or less volatile (methanol, ethanol, ethers, essential oils, etc.). In these cases it would be extremely difficult to develop direct or indirect gravimetric methods for the determination of the water content. In the determination of the water content of aliphatic organic solvents (e.g., alcohols, glacial acetic acid), one often makes use of the miscibility of the pure solvents with aromatic liquids such as xylene, benzene, and toluene. Water decreases the miscibility, and the mixture then becomes turbid. On heating the turbid mixture under suitable conditions, it becomes clear; and on cooling, an opalescence appears at a certain temperature, this temperature depending mainly upon the water content and to a lesser extent upon the ratio of mixing. This physico-chemical method provides a highly delicate means for the determination of traces of water in ethanol, methanol, glacial acetic acid, etc.

---

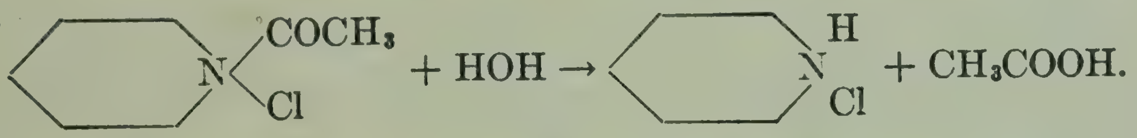
[1] In the most careful work the apparatus used and the procedure followed should be checked by running a control (p. 288) on a sample of known water content.

When water is present in organic material which is fairly volatile or which decomposes at temperatures at which the water is removed, another principle is often applied. The sample is distilled with an organic liquid (e.g., xylene) immiscible with water which has a boiling point of the order of 100°–150°. The distillate is collected in a graduated tube and the volume of the water read. This method is applicable to samples in which the water is loosely held and is often applied in the analysis of essential oils or organic materials decomposing at relatively low temperatures (flours, syrups).

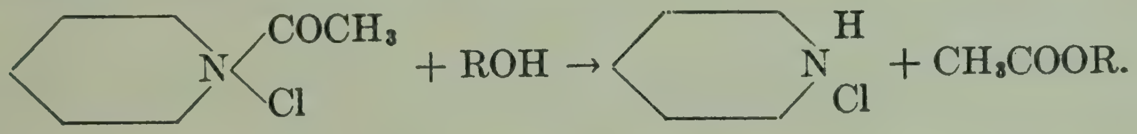
Methods based upon the occurrence of a quantitative chemical reaction between the water in the sample and an added substance are sometimes used in a water determination. Thus water reacts quantitatively with calcium carbide, $CaC_2 + H_2O \rightarrow CaO + C_2H_2$. From the amount of acetylene evolved (determined gasometrically or volumetrically), the amount of water present is calculated.[1] Bell [2] made use of the reaction between water and α-naphthoxydichlorphosphine:

$$C_{10}H_7OPCl_2 + 2\ H_2O \rightarrow C_{10}H_7OP(OH)_2 + 2\ HCl.$$

The hydrochloric acid formed is removed with a current of dry air, absorbed in water, and determined volumetrically with standard base. The method is suitable for the determination of water in nonhydroxylic organic solvents. More specific is the method proposed by Smith and Bryant,[3] which is based upon the reaction between acetyl chloride, pyridine, and water:



The excess of reagent (acetyl chloride) is removed with alcohol:



The acid is titrated with standard base, using phenolphthalein as indicator. The difference in the volumes between the actual determination and the blank indicates the amount of water.

A volumetric method for the determination of water in organic liquids and certain inorganic solids (including hydrated salts) has been devised by Fischer [4] and extended by others.[5] The sample is titrated with a methyl alcohol solution of iodine, sulfur dioxide, and pyridine to the appearance of the brown color of free iodine. If the salt-forming function of the pyridine is ignored for simplicity, the reaction may be represented as follows:

---

[1] See F. Henle, Ber. *53*, 719 (1920), who also reviews earlier methods.

[2] W. R. P. Bell, J. Chem. Soc. *1932*, 2903.

[3] D. M. Smith and W. M. D. Bryant, J. Am. Chem. Soc. *57*, 841 (1935).

[4] K. Fischer, Angew. Chem. *48*, 394 (1935).

[5] See, for example, D. M. Smith, W. M. D. Bryant, and J. Mitchell, J. Am. Chem. Soc. *61*, 2407 (1939); Bryant, Mitchell, Smith, and E. C. Ashby, *ibid. 63*, 2924 (1941); E. G. Almy, W. C. Griffin, and C. S. Wilcox, Ind. Eng. Chem., Anal. Ed. *12*, 392 (1940).

$$H_2O + I_2 + SO_2 + CH_3OH \rightarrow 2\ HI + CH_3HSO_4.$$

PROBLEM

Devise methods for determining:

(a) Hygroscopic water in ammonium chloride
(b) Total water in ferric chloride
(c) Hydrate water in $Ba(OH)_2 \cdot 8\ H_2O$
(d) Water content of strong sulfuric acid
(e) Water in sulfur dioxide gas.

CHAPTER XVII

DETERMINATION OF CHLORINE IN SOLUBLE CHLORIDES

Method.

Chlorine in a soluble chloride is determined gravimetrically by precipitation as silver chloride by the addition of an excess of silver nitrate solution to the chloride solution containing nitric acid:

$$Cl^- + Ag^+ \rightarrow AgCl.$$

The precipitate is collected in a filter crucible, washed with very dilute nitric acid to remove soluble salts, then dried at 100° to 200° and finally weighed as AgCl. The presence of nitric acid prevents the precipitation of silver salts insoluble in neutral medium (silver carbonate, silver phosphate, etc.).

Solubility of silver chloride.

The solubility of silver chloride in water is 1.8 mg. per liter at 25° and 21.1 mg. at 100°. In the presence of silver nitrate the solubility is of course much less (Chapter V). The optimum concentration of silver nitrate is stated to be 0.05 g. per liter;[1] such a solution will dissolve 0.05 mg. of silver chloride per liter at 20°. With greater concentrations of silver nitrate the solubility of the precipitate increases (cf. p. 56) but remains negligibly small as far as the requirements of ordinary careful analysis are concerned, even when the silver-ion concentration is 0.01 *M*. Therefore a moderately large excess of silver nitrate may be added in the precipitation. An unnecessarily large excess should be avoided.

Electrolytes not having an ion in common with a precipitate increase its solubility to a slight extent (p. 55). In accordance with this fact the solubility of silver chloride is increased by the nitric acid added in the procedure, and such salts as the alkali nitrates. The increase in the solubility of the precipitate from this source is so small that it introduces no error in ordinary analytical work if a small excess of silver nitrate is present. In the determination of atomic weights and other highly exact analytical work involving the precipitation and weighing of silver chloride, the amount of silver chloride remaining in solution after precipitation is allowed for and that dissolved by the wash liquid is determined nephelometrically (p. 688).[1]

---

[1] G. P. Baxter and F. A. Hilton, J. Am. Chem. Soc. *45*, 698 (1923).

Coagulation and aging of the precipitate. Adsorptive properties. Silver chloride is a good example of a colloidal precipitate. When first formed by precipitation in cold dilute solutions, it consists of extremely minute, partly agglomerated particles. The coagulation and the concomitant agglomeration as well as aging of the precipitate are especially promoted by heating and stirring the suspension in the presence of nitric acid and silver nitrate. The precipitate settles in heavy curdy masses, leaving a nearly clear supernatant liquid.

Although the precipitation of silver chloride is quantitatively complete almost immediately after the addition of silver nitrate, the suspension is always heated and allowed to stand for a few hours to complete the coagulation and permit the aging of the precipitate. On account of its finely divided character, silver chloride might be expected to adsorb appreciable amounts of foreign chloride or silver salts. Actually the precipitate shows very little tendency to adsorb foreign substances, even if aged at room temperature for only a few minutes after precipitation. Precipitated under analytical conditions, silver chloride does not carry down alkali or alkaline earth metal salts that may be present, nor silver nitrate, to any appreciable extent. The alkali content of a precipitate formed in a solution containing alkali salts is negligibly small.[2]

If silver chloride is washed with pure water, it may be peptized (p. 95). Some of the primary particles will then pass through the interstices of the filter and give a turbid filtrate. The peptization is easily prevented by using a dilute solution of nitric acid as the wash liquid. When the washed precipitate is dried, any nitric acid remaining adhering to it evaporates readily. The strength of the nitric acid wash solution need not be greater than 0.01 M. Higher concentrations should not be used, for the solubility of silver chloride is greater in the stronger nitric acid solutions.

Completeness of washing of the precipitate is tested for by determining whether the excess of the precipitating agent, silver nitrate, has been entirely removed. Hydrochloric acid is a suitable reagent for this purpose. One or two drops (not more) of 0.1 N acid is added to 3 to 5 ml. of the washings collected after the washing has been continued for some time. If the solution remains clear or shows only the slightest opalescence, all silver nitrate (and other soluble salts as well) has been washed out. It should be understood that a saturated solution of pure silver chloride will become opalescent when treated with a slight excess of silver nitrate or hydrochloric acid. Usually the wash liquid does not remain in contact with the precipitate for a sufficient length of time to become saturated with silver chloride, and therefore if the washings do not contain silver nitrate they will generally remain clear when tested with dilute hydrochloric acid in test tubes and in ordinary light.[1]

---

[1] See, for example, T. W. Richards and R. C. Wells, Pub. Carnegie Inst. of Washington, No. 28 (1905); G. P. Baxter and F. A. Hilton, J. Am. Chem. Soc. *45*, 695 (1923).

[2] G. F. Hüttig and E. Menzel, Z. anal. Chem. *68*, 354 (1926).

Effect of light on silver chloride.

Silver chloride is light sensitive; when exposed to light it is slowly decomposed into silver and chlorine, the silver remaining colloidally dispersed in the silver chloride and imparting a purplish-blue color to it. The chlorine largely escapes from the crystals. This decomposition proceeds quite rapidly in strong light (direct sunlight), and even in diffuse light it is appreciable. Account must be taken of this phenomenon in analytical work, or serious errors may result.

In the determination of chloride, the chlorine liberated photochemically from the precipitate reacts with the excess of silver nitrate present in solution and precipitates more silver chloride:

$$3\,Cl_2 + 3\,H_2O + 5\,Ag^+ \rightarrow 5\,AgCl + ClO_3^- + 6\,H^+.$$

The results would therefore be high under these conditions. If chloride is present in excess in the solution, as would be the case when *silver* is determined by precipitation with an excess of hydrochloric acid, the error would be negative, since then the chlorine simply escapes from the precipitate. Lundell and Hoffman,[2] who studied the effect of light on silver chloride from the analytical viewpoint, found that serious errors resulted if the solution containing the precipitate of silver chloride was exposed to strong light. Even when the precipitate was allowed to stand in reflected sunlight from a north window for three hours with occasional stirring, the results in a chloride determination were high to the extent of 0.2 per cent. The same authors also found that dried silver chloride very slowly lost weight when exposed to light. It is evident therefore that the operations must be carried out in light as subdued as possible and under no circumstances in direct sunlight. When the solution containing the precipitate is set aside, it should be placed in the dark (locker of desk) and not allowed to stand on the desk. In the most accurate work, daylight should be avoided entirely, and the operations conducted in red light. In ordinary careful analysis in which an accuracy of 0.1 per cent is satisfactory, the precipitation of silver chloride may be carried out in subdued daylight; but as already mentioned, the precipitate should not be allowed to stand unduly long in such light.

---

[1] In the case that the washings contain enough dissolved silver chloride to give an opalescence with dilute hydrochloric acid, completeness of washing is indicated by obtaining successive washings yielding equal turbidities.

[2] G. E. F. Lundell and J. I. Hoffman, Bur. Standards J. Research *4*, 109 (1930).

Drying the precipitate.

It has already been shown (p. 135) that it is not permissible in exact analytical work to dry and weigh a precipitate in filter paper. If filter paper is used for collecting the precipitate, it must finally be burned; and the residue then gives the weight of the ignited precipitate, provided the filter is "ashless." In the case of silver chloride, ignition of the precipitate in contact with the paper results in the reduction of more or less of the precipitate to free silver by the action of the carbon and reducing gases formed in burning off the paper. This difficulty can be overcome by separating as much as possible of the precipitate from the paper and reserving it while the paper is ignited. The small amount of silver chloride adhering to the paper is largely reduced to silver when the filter paper is burned and must be converted back to the chloride by successive treatment with nitric and hydrochloric acids. The main portion of the precipitate is then transferred to the crucible, and the whole is carefully heated to just below the fusion point of the substance.

This procedure is so time-consuming and subject to errors that it is much better to employ a filter crucible, in place of filter paper, to collect the precipitate. The crucible and its contents may then be heated in an electric oven to dry the precipitate. For many purposes drying at a temperature of 100° or slightly above gives a residue sufficiently free from water to yield satisfactory results. Experiments by the authors have shown that silver chloride dried to constant weight at 110° to 120° contains 0.03 to 0.04 per cent of water. It is stated [1] that silver chloride dried at 280° retains 0.01 per cent of water. To remove the last traces of water from silver chloride, it must be heated to the point of fusion (455°). The temperature must be carefully regulated in this operation for the substance volatilizes rapidly above its melting point, and even at the melting point it is slowly volatile; the presence of organic matter causes the reduction of silver chloride. In ordinary analysis, fusion of the silver chloride preparatory to weighing is not necessary The residue may be dried at 200° to 300° or even at 100° to 200° with satisfactory results. The dried residue is not appreciably hygroscopic. It has been proposed[1] to dry the precipitate without heating by washing it successively with alcohol and ether and allowing the latter to evaporate at room temperature. All the water is not removed in this way, but the results are not high by more than 0.1 per cent, so that the method is suitable for rapid work.

---

[1] Hillebrand and Lundell, *Applied Inorganic Analysis*, p. 164.

Interfering substances.

Anions which give silver salts insoluble in dilute nitric acid must, of course, be absent. These include bromide, iodide, thiocyanate, cyanide, ferrocyanide, ferricyanide, sulfide, and thiosulfate. Other anions such as carbonate, phosphate, chromate, arsenate, oxalate, etc., may be present, for the silver salts of these are soluble in the dilute nitric acid medium in which silver chloride is precipitated. In the presence of some of these anions (oxalate) it may be necessary to increase the nitric acid concentration in the solutions over that recommended in the procedure below.

Heavy metals may interfere, and if so it is necessary to remove them by appropriate methods before attempting to precipitate chloride. These metals may interfere in several ways:

1. They may hydrolyze in the dilute nitric acid solution and contaminate the silver chloride precipitate with their basic salts (antimony, bismuth, and tin, for example).
2. They may be coprecipitated with silver chloride (platinum and palladium, for instance).
3. They may prevent complete precipitation of silver chloride by forming complex or slightly ionized chlorides (mercuric mercury, chromium).

Substances which reduce silver nitrate in acid medium must be oxidized before precipitating the chloride (hypophosphite is an example). If the chloride is present in the nonionic form, as is the case in many organic compounds, the latter must be destroyed by a suitable procedure and the halogen transformed into the ionic state. Organic hydrophylic colloids such as gelatine and agar, which tend to keep the silver chloride in colloidal solution, have to be destroyed also. The procedure given below can, in general, be applied without modification only to the determination of chloride in the alkali and alkaline earth chlorides or hydrochloric acid solutions.

Procedure.[2] The following directions apply to the determination of chlorine in a soluble chloride containing no interfering substances.

Weigh out duplicate samples of 0.2 to 0.3 g. (or an amount containing approximately 0.1 g. of chlorine) into 250 or 300 ml. beakers provided with stirring rods and covered with watch glasses. Proceed with each sample as follows: Add approximately 150 ml. of water to the beaker, stir to dissolve the sample, and acidify with 1 ml. of 1 : 1 nitric acid.[1] The distilled water and nitric acid used should be tested for the presence of chloride with silver nitrate solution.

---

[1] J. Dick, Z. anal. Chem. 77, 352 (1929).

[2] Before beginning this determination, the student should read carefully Chapter XIV, dealing with the technique of precipitation, filtration, washing of precipitates, etc., and should refer to this chapter constantly during the determination for manipulative details.

Precipitate the chloride as silver chloride by slowly adding with stirring (p. 236) a slight excess of 0.1 N silver nitrate solution in the cold. If the chloride content of the sample is known approximately, calculate the volume of silver nitrate solution required, and add an excess of 5 to 10 ml. of 0.1 N silver nitrate over the calculated amount; otherwise assume that the sample is sodium chloride, and calculate the volume of precipitant required on this basis, again allowing an excess of 5 or 10 ml. *The precipitation and succeeding operations must be carried out in subdued daylight.*

After the silver nitrate solution has been added, heat the suspension nearly to boiling, and stir for a minute or two to aid the coagulation of the precipitate. Then remove the beaker from the heat, and allow the precipitate to settle. Test for complete precipitation of chloride by adding a few drops of silver nitrate solution to the supernatant liquid. If no further precipitate appears, set the beaker aside in the dark, and allow the solution to stand for at least 1 or 2 hours before filtration.

Collect the precipitate in a weighed filter crucible (Gooch, porcelain, or glass) which has been dried at the same temperature as is to be employed in heating the precipitate (*ca.* 100° to 200°), following the directions given on pp. 257–258 regarding the technique. Wash the silver chloride 2 or 3 times by decantation (p. 252) with cold 0.01 N nitric acid before transferring the precipitate to the crucible. Remove the last small particles of silver chloride from the beaker with a "policeman" (p. 253). Carefully examine the beaker to see that all of the precipitate has been removed. Wash the precipitate in the filter crucible with 0.01 N nitric acid, added in small portions as described on p. 258, until a few ml. of the washings collected in a test tube give no turbidity, or at most only a faint opalescence, when tested with 1 drop of 0.1 N hydrochloric acid. Finally wash the precipitate with 1 or 2 portions of water to remove most of the nitric acid.

---

[1] If the sample is alkaline, the solution must be neutralized with nitric acid, litmus paper being employed as indicator, and a slight excess added as above.

Heat the crucible and its contents to constant weight (p. 260) at 110° to 200°, following the directions on p. 261. Calculate the percentage of chlorine in the sample.

Other determinations based on the same principle.

Bromide, iodide, and thiocyanate can also be determined gravimetrically by precipitation with silver nitrate and weighing of the corresponding silver precipitate by methods closely resembling those for the determination of chloride. Moreover, the oxygen acids of the halogens (chlorate, bromate, etc.) can be determined by reducing them to the halides with a suitable reducing agent and precipitating with silver nitrate.

By using hydrochloric acid as precipitant, silver can be determined with great accuracy as the chloride. In this case the excess of hydrochloric acid used in the precipitation must be carefully regulated because of the marked solubility of silver chloride in too strong hydrochloric acid solutions (p. 60). Mercury is sometimes estimated by precipitation as mercurous chloride, but the results are somewhat low owing to the appreciable solubility of the precipitate in an excess of chloride and volatility of the precipitate at relatively low temperatures.

Determination of chlorine in insoluble chlorides.

If the chloride is insoluble, it is necessary to boil it with sodium carbonate solution or, better, to fuse it with sodium carbonate and extract the melt with water. In either case chloride goes into solution, and the filtrate is analyzed in the usual way after acidification with nitric acid. For the determination of chlorine in silicates, see p. 757.

PROBLEMS

1. What volume of 0.10 N silver nitrate is required to precipitate the chloride in 0.500 g. of NaCl? *Ans.* 85.5 ml.

2. (a) What is the maximum solubility loss that could result from washing a precipitate of silver chloride with 100 ml. of water at room temperature if $S_{AgCl} = 1.1 \times 10^{-10}$?

(b) Assuming that this loss occurs in the determination of chloride in 0.4422 g. of $BaCl_2 \cdot 2\,H_2O$, what are the absolute and the relative errors in the determination of chloride?

(c) Why will the actual loss be less than the calculated one?

Ans. (a) 0.00015 g.; (b) − 0.01 per cent absolute error, − 0.3 part per thousand relative error.

3. A 1.000 g. sample of alloy yielded 0.5721 g. of silver chloride. What is the percentage of silver in the alloy?

4. What weight of sample must be taken in the chloride determination in order that 1 mg. of AgCl shall represent 0.10 per cent of Cl? *Ans.* 0.247 g.

5. 0.2500 g. of an anhydrous mixture of sodium and potassium chlorides gave a dried silver chloride precipitate weighing 0.5248 g. Calculate the percentages of NaCl and KCl in the mixture.

Ans. 33.4 per cent NaCl, 66.6 per cent KCl.

6. A solution of potassium bromate was reduced to bromide and the latter precipitated with an excess of silver nitrate. If 0.4681 g. of AgBr was obtained, what was the weight of the $KBrO_3$ present? *Ans.* 0.4160 g.

7. Assuming theoretical conversion, what volume of 0.100 N silver nitrate solution can be obtained from 10.00 g. of pure silver chloride residues?

Ans. 698 ml.

8. What volume of silver nitrate solution containing the equivalent of 2.000 g. of silver per liter is required to precipitate the chloride and bromide in 0.5000 g. of a mixture containing 60.0 per cent NaCl and 40 per cent NaBr?

9. A silver chloride precipitate containing free silver as a result of exposure to strong light gave an apparent chloride content of 40.00 per cent in a salt. If the weighed residue contained 0.75 per cent of Ag, what is the absolute error resulting?

CHAPTER XVIII

DETERMINATION OF IRON

Method.

The solution containing iron in the *ferric*[1] state is treated with a slight excess of ammonium hydroxide to precipitate hydrous ferric oxide, $Fe_2O_3 \cdot x\,H_2O$. The precipitate is filtered off on paper, washed, ignited to ferric oxide, and weighed as such. Other elements that are precipitated by ammonium hydroxide must of course be absent.

Properties of hydrous ferric oxide.

The solubility of hydrous ferric oxide is not exactly known and, moreover, depends somewhat upon the way the substance has been precipitated. The solubility product $[Fe^{+++}][OH^-]^3$ is of the order of 10^{-36} or smaller. This figure indicates that the solubility in water is extremely small and explains why hydrous ferric oxide is quantitatively precipitated even from weakly acid media. If we work at room temperature and if the acidity corresponds to a pH of the order of 4, the hydroxyl-ion concentration of the solution is about 10^{-10}. Under equilibrium conditions: $[Fe^{+++}][OH^-]^3 < 10^{-36}$, and since $[OH^-] = 10^{-10}$, we find that the amount of iron left in the solution is smaller than corresponds to a concentration of 10^{-6} molar or 0.05 mg. Fe per liter. Evidently errors due to incomplete precipitation and solubility losses in washing will be negligibly small.

Since the solubility of the hydrous oxide is so extremely small, the relative supersaturation during the precipitation will be very great, and the precipitate formed will have a tremendous surface development. (Compare chapter on formation and properties of precipitates, especially p. 101.) As a matter of fact, the precipitate formed at room temperature by an excess of ammonia does not show an X-ray pattern; in other words, it is amorphous. If the hydrous oxide is precipitated at boiling temperature, the X-ray pattern shows very diffuse lines, indicating a crystalline structure; but the particles are of extremely small size, being far beyond the limit of microscopic visibility. Even on aging, the size of the particles increases but slowly. In other words, we have here a case in which the aggregation velocity is much greater than the orientation velocity (p. 101). The hydrous ferric oxide is a typical example of a flocculated colloid. The primary particles formed agglomerate to large aggregates which retain large amounts of water in the adsorbed state. For this reason it is better to consider the precipitate as a hydrous ferric oxide instead of hydrated ferric oxide, or ferric hydroxide containing a definite number of molecules of water.[1] Since the solubility of hydrous ferric oxide is so extremely small, the crystal size of the precipitate cannot be sensibly increased by adding the ammonium hydroxide very slowly to the iron solution, or vice versa; whether the reagent be added slowly or rapidly, the crystal size and filterability of the precipitate are about the same. The temperature of precipitation, however, is a most important factor in obtaining an easily filterable precipitate. The coagulation of a colloidal precipitate, and especially the agglomeration of the primary particles, is aided enormously by raising the temperature of the solution. Therefore the precipitation is made at or near the boiling point, and the liquid is kept at 100° for a short time after precipitation. The liquid should not be allowed to boil for any length of time after precipitation, for then the precipitate is liable to become slimy and difficult to filter, apparently as the result of partial breaking-up of the aggregates.

---

[1] Ferrous iron is not quantitatively precipitated by ammonium hydroxide in the presence of ammonium salts.

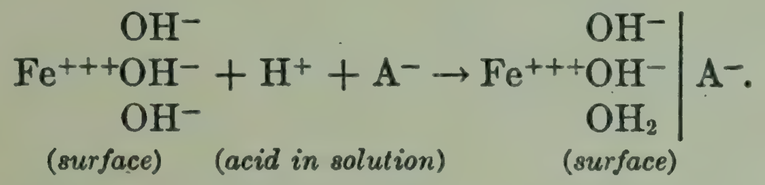
Filter paper is always used for the filtration of gelatinous precipitates such as hydrous ferric oxide. Suction filtration with filter crucibles results in the clogging of the crucible as the result of the forcing of the submicroscopic particles of these precipitates into the pores of the filtering medium. For the same reason the use of suction with paper filters should be avoided. The use of filter-paper pulp (p. 185) aids filtration and washing.

Because of their bulky nature the hydrous oxide precipitates are advantageously washed by decantation (p. 252). Hot water is a suitable wash liquid for hydrous ferric oxide, since the precipitate is not easily peptized. If the washing is likely to be long continued, a hot 1 per cent solution of ammonium chloride is recommended as a wash liquid, and will do no harm in any case. Under no circumstances may the precipitate be allowed to stand in the filter paper before complete washing, because it shrinks rapidly as it partially dries. As a result channels are formed in the precipitate; the wash liquid runs off through these, and thorough washing then becomes impossible. By virtue of its large surface development, hydrous ferric oxide (and other hydrous oxides as well) exhibits pronounced adsorptive properties.

---

[1] The terms *hydrous oxide* and *hydroxide* sometimes are used synonymously in this book. Strictly speaking, a metal hydroxide has a definite composition corresponding to the chemical formula, such as $Fe(OH)_3$, $Al(OH)_3$, etc. Precipitates of quadrivalent, trivalent, and many divalent metal hydroxides are never obtained as such, but in the form of highly voluminous hydrous oxides. These precipitates have no definite stoichiometric composition but consist of the metal oxide or hydroxide with variable amounts of water. The latter may be bound partly chemically and partly physically (adsorption), the total amount of water held by the precipitate depending upon the manner of precipitation and of aging before filtration. See H. B. Weiser, *The Hydrous Oxides*, McGraw-Hill Book Co., New York.

It should be realized that from solutions having an acid reaction there will be primarily an anion adsorption. The surface of the hydrous oxide attracts the protons (hydrogen ions), and consequently an equivalent amount of anion is adsorbed (see p. 95):

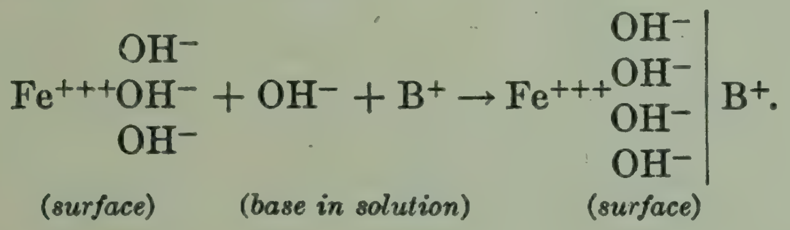


$$\begin{array}{rl} & \mathrm{OH^-}\\ \mathrm{Fe^{+++}} & \mathrm{OH^-}\\ & \mathrm{OH^-}\end{array} + \mathrm{H^+} + \mathrm{A^-} \rightarrow \left.\begin{array}{rl} & \mathrm{OH^-}\\ \mathrm{Fe^{+++}} & \mathrm{OH^-}\\ & \mathrm{OH_2}\end{array}\right| \mathrm{A^-}.$$

(surface) *(acid in solution)* *(surface)*

The adsorbability of the anions increases with increasing valence. Thus, for example, it is found that sulfate, chromate, and oxalate are much more strongly adsorbed than chloride, nitrate, etc. In addition, the adsorption increases with increasing hydrogen-ion concentration. Therefore a coprecipitation of anions can be expected if the precipitate is formed in acid medium. This is actually the case. On very slow addition of ammonium hydroxide to a solution of a ferric salt, a coprecipitation of anions occurs, because the solution remains acid as a result of the strong hydrolysis of the ferric ions as long as some of these remain in the solution. The coprecipitated anions are more or less rapidly given off again in the presence of an excess of ammonia.

In ammoniacal, or quite generally in alkaline, media, the hydrous ferric oxide has a tendency to adsorb hydroxyl ions with the result that an equivalent amount of cation is carried down:



$$\begin{array}{rl} & \mathrm{OH^-}\\ \mathrm{Fe^{+++}} & \mathrm{OH^-}\\ & \mathrm{OH^-}\end{array} + \mathrm{OH^-} + \mathrm{B^+} \rightarrow \mathrm{Fe^{+++}}\left.\begin{array}{l} \mathrm{OH^-}\\ \mathrm{OH^-}\\ \mathrm{OH^-}\\ \mathrm{OH^-}\end{array}\right| \mathrm{B^+}.$$

(surface) *(base in solution)* *(surface)*

Therefore in precipitation from ammoniacal medium there may be a pronounced coprecipitation of cations. The adsorbability of the cations increases with decreasing solubility of their hydroxides and with their valence. Thus calcium, magnesium, copper $[\mathrm{Cu(NH_3)_4^{++}}]$, zinc $[\mathrm{Zn(NH_3)_4^{++}}]$, etc. are much more strongly adsorbed and coprecipitated than sodium, potassium, and ammonium. A large excess of ammonia decreases the adsorption and coprecipitation of other cations. There is competition between the ammonium and other cations to be adsorbed; increase of the ammonia concentration therefore favors the adsorption of the ammonium ions at the cost of that of the other cations. Much more effective is the combination of a small excess of ammonia with large amounts of ammonium salts. Under these conditions the replacing effect of the ammonium ions is so great that the adsorption and coprecipitation of divalent cations can be reduced to extremely small values in many instances.

Properties of ferric oxide.

When hydrous ferric oxide is strongly heated (800° to 1000°), it is converted into ferric oxide:

$$Fe_2O_3 \cdot x\,H_2O \rightarrow Fe_2O_3 + x\,H_2O.$$

The ignition of the precipitate should be made under good oxidizing conditions, especially during the burning of the paper filter, for otherwise there may be a partial reduction of ferric oxide by carbon or reducing gases to the magnetic oxide, Fe_3O_4, or even to the metal. These reduction products can be converted back to ferric oxide by continued heating of the residue with free access of air, although the reoxidation may be slow if much of the magnetic oxide has been formed. Care should be taken to exclude reducing gases from the flame during the ignition (p. 259). When a platinum crucible is used for the heating, there is possibility of transfusion of hot reducing gases through the walls of the vessel when a flame is used.

On strong heating, ferric oxide is decomposed into the magnetic oxide and oxygen:

$$6\,Fe_2O_3 \rightleftarrows 4\,Fe_3O_4 + O_2.$$

Fortunately a very high temperature must be attained before this decomposition becomes analytically significant. Baxter and Hoover[1] found that a sample of pure ferric oxide heated in air to constant weight at approximately 1100° lost in weight to the extent of only 0.004 per cent, corresponding to the formation of 0.12 per cent Fe_3O_4. The magnetic oxide resulting forms a solid solution with the ferric oxide,[2] and consequently the oxygen pressure of the system at equilibrium depends upon the ratio of ferrous iron to ferric in the solid phase (contrast this system with the $CaCO_3$—CaO—CO_2 system, p. 351). At higher temperatures the extent of the decomposition is greater. This solid-solution formation also explains why the reoxidation of the magnetic oxide formed during the ignition of the hydrous oxide is such a slow process.

Ferric oxide is rendered water-free by ignition at 1000°. The precipitate can be satisfactorily ignited in a covered porcelain or platinum crucible over a Tirrill burner. The residue thus obtained is not appreciably hygroscopic, in contrast to aluminum oxide, which requires ignition at the minimum temperature of 1200° to render it water-free and non-hygroscopic (p. 325).

Often it is necessary to obtain the combined weight of ferric oxide and aluminum oxide in a sample. Thus, in determining aluminum and iron in the presence of each other, the metals are precipitated as the hydrous oxides and ignited to the oxides; the weight of the ignited mixed oxides is obtained, the iron in the residue is determined by a volumetric method, and the aluminum is then found by difference (see, for example, p. 744). In such cases the choice of a proper ignition temperature for the mixed oxides of aluminum and iron is an important matter. If the temperature is too low, the aluminum oxide is not rendered water-free, because it tenaciously retains water, as already stated, up to temperatures of 1200° or slightly higher. On the other hand, if the ignition temperature is too high, there is danger of converting some of the ferric oxide into the magnetic oxide of iron; and it appears [1] that this decomposition can be analytically important at 1200°.

---

[1] G. P. Baxter and C. R. Hoover, J. Am. Chem. Soc. *34*, 1657 (1912).

[2] R. B. Sosman and J. C. Hostetter, J. Am. Chem. Soc. *38*, 807, 1188 (1916).

It is sometimes stated that a precipitate of hydrous ferric oxide containing chloride (as from a wash solution of ammonium chloride) loses iron on ignition as the result of the volatility of ferric chloride at high temperatures. It has been shown that such losses do not take place if only small amounts of chloride are present.[2] It is perfectly safe to ignite a precipitate of iron which has been washed with a 1 per cent solution of ammonium chloride without first washing out most of the chloride.

Interfering substances. Separations.

Other elements that are precipitated by ammonium hydroxide, such as aluminum, trivalent chromium, titanium, zirconium, and many of the less common elements, must be absent in a solution in which iron is to be determined gravimetrically. Anions such as phosphate, arsenate, vanadate, and silicate, which yield insoluble salts of iron in weakly basic media, must likewise be absent. Silica is a very common contaminant of the hydrous ferric oxide precipitate; it may be derived from the ammonium hydroxide used in the precipitation, or it may be taken up from the glass vessels during the precipitation.

The presence of certain substances which form complexes with ferric iron from which the metal cannot be precipitated with ammonium hydroxide must be guarded against. Included among these substances are organic hydroxy-compounds such as hydroxy-acids (tartaric, citric, etc.) and sugars. These can be destroyed by igniting the sample or by oxidation with an appropriate reagent in solution. Of the inorganic acids forming stable complexes with ferric iron, there may be mentioned pyrophosphoric and hydrofluoric acids.

In the presence of the divalent metals precautions must be taken to prevent the coprecipitation, or even precipitation, of these hydroxides when precipitating ferric iron with ammonium hydroxide. With some of these metals, however, a satisfactory separation cannot be made. Generally in these cases a high concentration of ammonium salt in the solution has a very favorable effect. The decrease in the coprecipitation of such metals as magnesium and calcium under these conditions is to be attributed largely to the replacing effect of the ammonium ion (p. 119). No particular difficulty is encountered in separating ferric iron by ammonia precipitation from the alkali and alkaline earth metals[1] as well as magnesium if a sufficient amount of ammonium salt is present; a double precipitation gives a hydrous ferric oxide practically free from these metals (in the presence of much magnesium a triple precipitation may be required). Likewise a satisfactory separation of iron from nickel and manganese can be made if care is taken to limit to a minimum the excess of ammonium hydroxide added.[2] The separation from copper, zinc, and cobalt by the addition of a large excess of ammonium hydroxide is not satisfactory.

---

[1] K. Zimmermann, Chem. Weekbl. *31*, 317 (1934), claims that ferric oxide is decomposed to a very appreciable extent even at 1050°.

[2] H. W. Daudt, J. Ind. Eng. Chem. 7, 847 (1915).

It may be mentioned here that precipitation of iron by the basic acetate method (p. 71) serves to separate the metal satisfactorily from zinc, nickel, cobalt, and manganese under the proper conditions.[3] By double precipitation with ammonium benzoate in hot, weak acetic acid medium, good separations of iron from zinc, manganese, nickel, cobalt, calcium, and magnesium can be effected.[4]

Determination of iron in ferrous ammonium sulfate.[5]

Procedure. Weigh out two 1.0 g. samples of ferrous ammonium sulfate hexahydrate (or a sufficient amount of other sample to contain 0.15 to 0.2 g. of iron) into 400 ml. Pyrex beakers provided with stirring rods and cover glasses. Dissolve each portion in 40 or 50 ml. of water and 10 ml. of 1 : 1 hydrochloric acid. Heat the solutions to boiling, and treat each as follows: Measure out 1 ml. of concentrated (16 N) nitric acid[6] in a 5 or 10 ml. graduate, and add it dropwise with stirring to the solution, which should be boiling only gently. The solution will first become dark, owing to the formation of the compound $FeSO_4 \cdot NO$; but this soon decomposes, leaving a yellow solution. Continue to boil the solution gently until it is clear yellow. Usually boiling for 3 to 5 minutes is sufficient. At this point it is well to test the solution for the complete oxidation of the iron. Transfer a drop of the solution to a test tube by means of a stirring rod, and dilute it with about 1 ml. of water. Place a small drop of the mixed diluted solution on a spot plate, and add a drop of freshly prepared 0.01 to 0.02 per cent potassium ferricyanide solution. If a blue color appears, ferrous iron is still present in the solution, and more nitric acid must then be added to the solution in the beaker and the boiling continued to complete the oxidation. Rinse the solution remaining in the test tube into the beaker.

---

[1] When calcium or other alkaline earth metals are present, it is important to use carbonate-free ammonium hydroxide for the precipitation of iron (and other metals precipitable by ammonia), else calcium carbonate may be precipitated.

[2] G. E. F. Lundell and H. B. Knowles, J. Am. Chem. Soc. *45*, 676 (1923).

[3] A method for the separation of aluminum (and presumably iron) from these metals, involving the slow neutralization of an acid solution by the hydrolysis of urea, is mentioned by Willard and Furman, *Elementary Quantitative Analysis*.

[4] I. M. Kolthoff, V. A. Stenger, and B. Moskovitz, J. Am. Chem. Soc. *56*, 812 (1934).

[5] The sample may be pure $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6\ H_2O$ (Mohr's salt), or it may be an effloresced product probably containing some iron in the ferric state. The directions given above are applicable to the analysis of any pure iron salt or any mixture which is soluble in water or dilute acid, which does not contain any other element that is precipitated by ammonium hydroxide, and which is not appreciably coprecipitated (p. 319). For the separation of iron from the divalent metals, certain modifications in procedure must be made (see above). Moreover, if sulfate is to be determined in the same sample, the method of precipitation must be altered (p. 317).

[6] Instead of nitric acid, bromine water or pure hydrogen peroxide may be used to oxidize the ferrous iron. The latter reagent is conveniently used in the form of 30 per cent solution (perhydrol); 1 ml. of this solution is sufficient for the oxidation. The excess of the reagent should be destroyed by boiling the solution.

If all the iron is found to be in the ferric state, dilute the solution to 200 ml., heat nearly to boiling, and add pure 1 : 1 ammonium hydroxide in a slow stream from a small beaker, stirring constantly, until a slight excess of reagent is present, as shown by the odor of the liquid after blowing away the fumes.[1] Remove the beaker from the heat, and allow the precipitate to settle. Then decant the supernatant liquid through a 9 cm. ashless filter paper of loose texture (e.g., S. and S. 589, black band) well fitted to the funnel, being careful to leave as much as possible of the precipitate in the beaker. Wash the precipitate three or four times by decantation (p. 252) with hot water, using 75 to 100 ml. each time. Then transfer the hydrous ferric oxide to the filter (p. 253) with the aid of a "policeman" (p. 193). Dislodge all particles of precipitate from the walls of the beaker, and add them to the main portion. Finally examine the beaker carefully for any remaining precipitate. Wash the precipitate on the filter (p. 256) with hot water until the washings give no reaction, or at most only a slight one, with silver nitrate acidified with nitric acid.[2]

If it is convenient, set the filter and its contents aside at this point to drain and partially dry overnight. This air-drying is by no means necessary, but it saves time in the subsequent slow heating of the precipitate in the crucible to expel water. Fold over the edge of the filter paper, and place the filter and its contents in a weighed porcelain crucible. Proceeding as described on p. 259, heat the crucible with the low flame of a Tirrill burner to expel the water, taking great care to avoid the sudden expulsion of steam, which would be almost certain to lead to losses of precipitate. When the precipitate is dry, char the paper below a red heat, and burn off the carbon at as low a temperature as possible, following the directions given on p. 260. Increase the heat of the burner to the full when all the carbon has been burned away, and maintain the crucible at this temperature for 15 minutes. Take care to exclude the gases of the flame from the interior of the crucible. Allow the crucible to cool below redness, and then place it covered in a desiccator. After 30 minutes weigh the crucible and its contents, and repeat the ignition to constant weight (0.2 mg.), employing 10- or 15-minute periods of heating.

---

[1] At this point it is advantageous, but not necessary, to add a little ashless filter-paper pulp to aid the filtration and washing of the precipitate (p. 185). One fourth of a Schleicher and Schüll filter-pulp tablet disintegrated by shaking with water in a test tube furnishes sufficient suspension for one sample. The addition of paper pulp is of greater importance when the ignited residue must subsequently be brought into solution, as in rock analysis (p. 737).

[2] Naturally this thorough washing is not called for in the analysis of pure ferrous ammonium sulfate or other samples not containing appreciable amounts of non-volatile matter.

Calculate the percentage of iron in the sample from the weight of Fe_2O_3 obtained.

Other metals determined by precipitation as hydrous oxides.

Of the more common metals the following can be quantitatively precipitated by ammonium hydroxide: aluminum, chromium (trivalent), titanium (quadrivalent), and zirconium.[1] The precipitates can be ignited to the corresponding oxides Al_2O_3, Cr_2O_3, TiO_2, and ZrO_2. In the case of aluminum and chromium the pH of the solution must be adjusted rather carefully because the hydroxides of these metals, being amphoteric, are somewhat soluble in ammonium hydroxide. The precipitation of hydrous aluminum oxide is considered at greater length in Chapter XIX. The gravimetric determination of chromium possesses the disadvantage that the precipitate must be ignited in hydrogen when results of the highest accuracy are desired. Chromic oxide when strongly heated in air gives small amounts of $Cr_2(CrO_4)_3$ with consequent high results. It is much better to determine chromium volumetrically by oxidizing to chromic acid and titrating the latter (see, for example, p. 723).

---

[1] In the presence of an oxidizing agent such as bromine or ammonium persulfate, divalent manganese can be quantitatively precipitated as hydrous manganese dioxide by ammonia. On ignition the precipitate can be made to give a residue approximating the composition Mn_3O_4. Since the composition of the ignition residue is variable even under rather carefully regulated conditions, this method of determining manganese is not often applied.

PROBLEMS

1. A 1.000 g. sample of partially effloresced ferrous ammonium sulfate yielded a residue of Fe_2O_3 weighing 0.2140 g. after strong ignition. What was the percentage of water in the sample? *Ans.* 23.86 per cent.

2. Assuming that $[Fe^{+++}][OH^-]^3 = 10^{-36}$, calculate the iron concentration in an aqueous solution of pH 4.5 in equilibrium with $Fe(OH)_3$. $K_w = 10^{-14}$. *Ans.* 3×10^{-8} *M*.

3. A determination of iron in a sample, based on the weighing of Fe_2O_3, gave a value of 10.11 per cent Fe. If the ignited precipitate contained 3.00 per cent of Fe_3O_4, what is the true percentage of Fe in the sample? *Ans.* 10.12 per cent.

4. (a) What volume of bromine water (3.5 g. bromine in 100 ml. of solution) is theoretically required to oxidize the iron in 1.000 g. of $FeCl_2 \cdot 4\,H_2O$?
(b) What volume of 16 *M* nitric acid is required to oxidize the iron in 1.000 g. of $FeSO_4 \cdot 7\,H_2O$? Assume reduction of nitric acid to NO. *Ans.* (a) 11.5 ml.

5. An oxide of iron contains 24.12 per cent of iron in the ferrous state and 48.24 per cent in the ferric state. What is its formula?

CHAPTER XIX

DETERMINATION OF ALUMINUM

The two important methods for the determination of aluminum are:

1. Precipitation as hydrous aluminum oxide and weighing as Al_2O_3.
2. Precipitation with 8-hydroxyquinoline and weighing the precipitate as such.

I. Determination as oxide.

The determination of aluminum by precipitation of hydrous aluminum oxide and the ignition of the latter to aluminum oxide is subject to three important sources of error: (1) the solubility of hydrous aluminum oxide in a too large excess of the precipitant, ammonium hydroxide; (2) the hygroscopicity of the ignited oxide; (3) coprecipitation of foreign metal hydroxides which are normally soluble in ammonium hydroxide.

The quantitative precipitation of hydrous aluminum oxide by ammonium hydroxide. Blum,[1] who made a careful study of the determination of aluminum as oxide, found that the precipitation of the hydrous oxide begins at pH 3, is complete at or before pH 7, and that the re-solution of the precipitate begins to be sensible at pH 9. It will be seen that ammonium hydroxide may not be added in uncontrolled excess, or the results may be low. By employing a suitable indicator, it is a simple matter to adjust the pH of the solution to the proper value. Phenol red [2] is an excellent indicator for the purpose [pH range, 6.4 (yellow) to 8.0 (red)].

Aluminum hydroxide (or hydrous aluminum oxide) has acid as well as basic properties; in other words it behaves as an amphoteric substance:

$$Al(OH)_3 + 3\,H^+ \rightarrow Al^{+++} + 3\,H_2O \qquad (1)$$
$$Al(OH)_3 + OH^- \rightarrow AlO_2^- + 2\,H_2O. \qquad (2)$$

According to reaction (1) the hydroxide dissolves in acid with the formation of aluminum ions. If the hydroxide is present as a solid body, it is easily seen that the solubility increases with the third power of the hydrogen-ion concentration:

$$\frac{[Al^{+++}]}{[Al(OH)_3][H^+]^3} = K,$$

or

$$\frac{[Al^{+++}]}{[H^+]^3} = K'.$$

or

$$[Al^{+++}] = [H^+]^3\,K'$$

---

[1] W. Blum, J. Am. Chem. Soc. *38*, 1282 (1916).

[2] J. N. Frers, Z. anal. Chem. *95*, 119 (1933).

On the other hand, in alkaline medium the solubility increases in proportion to the hydroxyl-ion concentration or inversely as the hydrogen-ion concentration. From equation (2) we find:

$$[\mathrm{AlO_2^-}] = [\mathrm{OH^-}]K'' = K''K_w \frac{1}{[\mathrm{H^+}]}.$$

Evidently then there must be a hydrogen-ion concentration at which the aluminum hydroxide has a minimum solubility. The pH corresponding to this minimum solubility is called the *isoelectric point.* It is not sharply defined for aluminum hydroxide but lies in the pH range between about 6.5 and 7.5. From the above it is clear that the excess of ammonia used to precipitate aluminum must be regulated.

A comparatively large amount of ammonium chloride should be present in the solution during the precipitation. On the one hand, the buffering action of the ammonium salt enables the adjustment of the pH to the optimum value to be made more easily, and, on the other hand, the salt aids in the coagulation of the precipitate. Furthermore, a sufficient quantity of ammonium salt minimizes the coprecipitation of divalent metals such as calcium and magnesium, since the ammonium ion has a replacing effect upon the other cations. In order to obtain an easily filterable precipitate, the precipitation is made in hot solution. The precipitate must not be washed with water, for then the hydrous aluminum oxide is peptized and will run through the filter. A dilute solution of ammonium chloride made basic to phenol red with ammonium hydroxide is a suitable wash liquid.

The ignition of the precipitate. The aluminum oxide formed by the ignition of hydrous aluminum oxide has the disagreeable property of being very hygroscopic unless it has been heated to a very high temperature. As far as the temperature necessary for complete expulsion of moisture from the oxide is concerned, Blum [1] found that a precipitate ignited in platinum over a blast lamp at a temperature of 1100° to 1150° for five or ten minutes did not lose in weight when further heated at 1450° for three ten-minute intervals, correction being made for the loss in weight of the platinum crucible and great care being taken to prevent adsorption of moisture during cooling and weighing. However, the oxide ignited at 1100° to 1150° is hygroscopic. If the ignition temperature is raised to 1200° or above, the residue obtained is not hygroscopic [2] and may be weighed at leisure.[3]

---

[1] W. Blum, *loc. cit.;* cf., however, W. Miehr, P. Koch, and J. Kratzert, Z. angew. Chem. *43*, 250 (1930).

[2] J. N. Frers, Z. anal. Chem. *95*, 131 *et seq.* (1933).

[3] Then, however, according to Frers, the hygroscopicity of the *porcelain* crucible must be taken into consideration. This author found that porcelain crucibles strongly ignited were sensibly hygroscopic; and therefore an error was likely to be made if they were weighed immediately after removal from the desiccator, because the change in weight due to adsorption of water is greatest when they are first exposed to the air. Frers, therefore, recommends cooling the crucible for one hour in the desiccator and then letting it stand for ten minutes in the balance before weighing. Evidently this procedure can be followed only when the ignited residue is entirely non-hygroscopic.

The marked decrease in hygroscopicity of the precipitate when heated above 1200° is due to the rapid transformation of the γ-form of aluminum oxide (the form obtained by heating hydrous aluminum oxide below 1000°) into another form, α-aluminum oxide (corundum).

The statement which is sometimes made that hydrous aluminum oxide containing chloride (as from the wash solution) loses aluminum chloride on ignition has no basis in fact. Precipitates formed in solutions containing sulfate are contaminated with basic aluminum sulfate, and this substance must be strongly heated to decompose it into aluminum oxide and sulfur trioxide. Whereas hydrous aluminum oxide containing no sulfate can be heated to constant weight at 1200° in approximately ten minutes, a precipitate containing moderate amounts of sulfate will require a half-hour ignition at the same temperature to effect the same result.

Coprecipitation with hydrous aluminum oxide. Aside from the fact that many other elements are quantitatively precipitated by ammonium hydroxide, it is necessary to bear in mind when precipitating hydrous aluminum oxide that a number of metal hydroxides or hydrous oxides are carried down by the precipitate. Cobalt, copper, zinc, nickel, and some other hydroxides are partially precipitated at the pH required to precipitate aluminum quantitatively. A reprecipitation does not give a pure precipitate when appreciable amounts of these metals are present.

Under the conditions specified in the procedure below, satisfactory separations of aluminum from the alkalies,[1] calcium, barium, strontium, and magnesium can be made, especially if the precipitate is dissolved and reprecipitated. Magnesium is the most strongly coprecipitated of these. Blum [2] found that when precipitated under conditions similar to those recommended below, 0.1 g. of aluminum oxide contained less than 1.0 mg. of magnesium oxide, when the equivalent of 0.2 g. of magnesium oxide was present. A second precipitation reduces the amount of magnesium to negligible proportions. It is especially important to have sufficient ammonium chloride in solution when magnesium is present.

In the presence of cobalt, zinc, and nickel, it is best to precipitate aluminum as the basic benzoate in slightly acid solution (p. 71). By two precipitations (sometimes one suffices) the aluminum can be obtained virtually free from the divalent metals.

The determination of aluminum in the complex precipitate obtained with ammonium hydroxide when other precipitable elements are present is described on page 744.

Procedure. To 200 ml. of solution containing a suitable weight of sample, add 4 to 5 g. of pure ammonium chloride and 0.5 ml. of 0.1 per cent solution of phenol red. Heat the solution nearly to boiling, and add pure dilute (1 : 1) ammonium hydroxide dropwise until the color changes from yellow to orange. Keep the liquid at the boiling point for 2 or 3 minutes, and then filter through a loose-textured paper. Wash the precipitate with a hot 2 per cent solution of ammonium chloride made neutral with ammonia against phenol red. If necessary dissolve the precipitate in hot 1 : 1 hydrochloric acid and reprecipitate. Place the paper with the precipitate in a weighed platinum or porcelain crucible, dry, char the paper and burn off the carbon, and then ignite the residue in a furnace at 1200° or, less preferably, over a blast lamp.[1] Heat for 10-minute periods until constant weight is attained. While the oxide should not be sensibly hygroscopic if the temperature of the ignition has been 1200° or above, it is wise to observe the usual precautions called for in the weighing of hygroscopic substances. Cool the crucible in a desiccator charged with sulfuric acid or other effective desiccant, and keep it covered at all times.

---

[1] With small amounts of alkalies present a single precipitation will usually suffice, but when large amounts are in solution, as for example after a potassium pyrosulfate fusion, double precipitations must be made.

[2] W. Blum, *loc. cit.*

II. Determination of aluminum by precipitation with 8-hydroxyquinoline.

From an acetic acid solution buffered with acetate, a solution of 8-hydroxyquinoline (p. 78) in acetic acid quantitatively precipitates aluminum as $Al(C_9H_6ON)_3$. The precipitate can be weighed as such after drying at 100° to 150°; it may also be ignited to the oxide, but this is usually disadvantageous. Even in pure solutions this method of determining aluminum has advantages over the ammonia precipitation. The precipitate is crystalline and therefore is more easily filtered than hydrous aluminum oxide. It can be dried at a low temperature, it is not hygroscopic, and the low percentage of aluminum in the weighing form is a distinct advantage.

By the use of this organic reagent a number of important separations of aluminum from other substances can be effected. By precipitation in faintly acid solution, aluminum is separated from the alkalies, magnesium, calcium, and beryllium;[2] in ammoniacal solutions from phosphorus, arsenic, fluorine, and boron; in ammoniacal solutions containing hydrogen peroxide from tantalum, columbium, titanium, and molybdenum; and in ammonium carbonate solution from uranium.[3] On the other hand, in solutions containing tartrate, such metals as copper, cadmium, zinc, and magnesium are precipitated by 8-hydroxyquinoline, while aluminum is not.[4]

Procedure for precipitation of aluminum by 8-hydroxyquinoline in pure solutions or those containing only the alkalies, alkaline earths, or magnesium.

Reagent: 5 per cent solution of 8-hydroxyquinoline in 2 *N* acetic acid.

To a warm solution (70° to 80°) very slightly acid with hydrochloric or sulfuric acid and containing not more than the equivalent of 0.05 g. aluminum per 100 ml., add a slight excess of the reagent, allowing 1 ml. for each 3 mg. of aluminum present. Slowly add 2 *N* ammonium acetate solution until a precipitate forms (if one has not already formed), and then add 25 ml. more for each 100 ml. of solution to insure complete precipitation. If the supernatant liquid is yellow, enough reagent has been added. Allow the liquid to stand for an hour without further heating, and collect the precipitate in a filter crucible. Wash the precipitate well with cold water, and dry at 120° to 140°. The dried precipitate has the composition $Al(C_9H_6ON)_3$ and contains 11.10 per cent of Al_2O_3. The precipitate can also be titrated (p. 638).

---

[1] If the ignition is made over a blast lamp, a platinum crucible should be used.

[2] I. M. Kolthoff and E. B. Sandell, J. Am. Chem. Soc. *50*, 1900 (1928).

[3] Separations in ammoniacal solution are described by G. E. F. Lundell and H. B. Knowles, Bur. Standards J. Research *3*, 91 (1929).

[4] R. Berg, Z. anal. Chem. *71*, 370 (1927).

PROBLEMS

1. A 0.5000 g. sample containing aluminum in the form of bauxite yielded 0.2508 g. of Al_2O_3. Calculate the percentage of bauxite, assuming its formula to be $Al_2O_3 \cdot 2\ H_2O$. *Ans.* 67.89 per cent.

2. A 0.5047 g. mixture of ferric oxide and aluminum oxide was found to contain 0.0946 g. of Fe. Calculate the weight of Al_2O_3 in the mixture. *Ans.* 0.3694 g.

3. A 1.000 g. sample containing 10 per cent Fe^{III}, 5 per cent Al, and 2 per cent Ti was brought into solution, the metals precipitated as hydroxides, and the washed precipitate ignited to the oxides. What was the weight of the residue?

4. What weight of sample must be taken in order that each mg. of aluminum hydroxyquinolate shall represent 0.10 per cent Al_2O_3?

CHAPTER XX

DETERMINATION OF SULFUR AS BARIUM SULFATE

Method.

A dilute solution of barium chloride is added to the solution containing sulfur as sulfate to precipitate barium sulfate:

$$SO_4^{=} + Ba^{++} \rightarrow BaSO_4.$$

The precipitation is made in a solution slightly acidified with hydrochloric acid and near the boiling temperature. The precipitate is filtered off, washed with water, ignited at redness, and weighed as barium sulfate.

Solubility of barium sulfate. Functions of hydrochloric acid in the procedure.

The solubility of barium sulfate in water is very small, amounting at room temperature to 0.3 or 0.4 mg. per 100 ml. of saturated solution. Mineral acids increase the solubility very appreciably (p. 61). Some values for the solubility of barium sulfate in hydrochloric acid solutions of different concentrations are given in Table XLVI.

TABLE XLVI. SOLUBILITY OF BARIUM SULFATE IN HYDROCHLORIC ACID SOLUTIONS AT ROOM TEMPERATURE [1]

NORMALITY OF HYDROCHLORIC ACID	MG. OF $BaSO_4$ IN 100 ML. SATURATED SOLUTION
0.00	0.4
0.10	1.0
0.30	2.9
0.50	4.7
1.00	8.7

The presence of a small amount of hydrochloric acid in the solution in which barium sulfate is precipitated is required to prevent the possible precipitation of the barium salts of such anions as carbonate and phosphate which are insoluble in neutral or basic solutions; moreover the coprecipitation of barium hydroxide is prevented by carrying out the precipitation in a slightly acid medium. The presence of hydrochloric acid has the further important effect of promoting the formation of a coarse, easily filterable precipitate. Barium sulfate precipitated in neutral solutions, even when these are dilute, is likely to be so fine-grained that it will run through the filter. Since the solubility of barium sulfate is greater in acid than in neutral solutions, fewer nuclei are formed when the precipitation is made in the presence of hydrochloric acid, and consequently the final crystals will then be of larger size (p. 99). It is of great importance to make the precipitation at boiling temperature, for the relative supersaturation is less at higher temperatures. The concentration of hydrochloric acid that may be used is limited by the solubility of barium sulfate in the acid medium. It has been found that a hydrochloric acid concentration of approximately 0.05 N is suitable. In the presence of an excess of barium chloride the solubility of the precipitate is very small at this acidity. The precipitate may be washed with cold water. Except in the most exact work, the loss of barium sulfate by solubility in the wash water may be neglected.

---

[1] Z. Karaoglanow, Z. anal. Chem. *56*, 241 (1917). The exact temperature of saturation is not specified.

Since barium sulfate is not freely soluble in any acid except hot concentrated sulfuric acid, it is not feasible to purify the precipitate by reprecipitation.

Coprecipitation with barium sulfate.

Barium sulfate provides a notorious example of a precipitate subject to contamination through the action of coprecipitation phenomena. Since the determination of sulfate is of great practical importance, a great deal of attention has been paid to the problem of obtaining a pure precipitate of barium sulfate; and hundreds of papers on the subject are to be found in the literature. In spite of the immense amount of work that has been done, the determination of sulfate remains one of the less accurate determinations of quantitative analysis.

In this section we shall confine ourselves to a brief general consideration of the subject of coprecipitation with barium sulfate and reserve a more detailed examination of the matter, especially with reference to the minimization of the associated errors, to the next section.

Precipitated under analytical conditions, barium sulfate yields a microcrystalline precipitate. The contaminating substances are largely present in the interior of the crystals and not at the external surface. We are dealing here with a case of *occlusion* of foreign substances (p. 111), this occlusion being the result of the incorporation in the crystals of ions or molecules adsorbed during the growth of the precipitate. From the analytical point of view the coprecipitation of the following are important:

1. Foreign anions: chloride, nitrate, and chlorate. These are coprecipitated as the corresponding barium salts.
2. Foreign cations: hydrogen, the alkali metals, calcium, and ferric iron. These are coprecipitated as the sulfates or bisulfates.
3. Water: water is occluded and adsorbed by barium sulfate. On ignition all the water is driven off provided that the temperature of heating is high enough. Precipitates dried at 105° to 120° may contain several tenths of a per cent of water.

In general, the phenomena of coprecipitation observed with barium sulfate are in accord with the predictions of the theory of coprecipitation (p. 120). In studying the contamination of barium sulfate, the influence of such factors as the specific adsorbability of the ions in question, the concentration and temperature of the solutions, the manner of addition of the precipitant, and the treatment of the precipitate after its formation must all be considered.

Barium sulfate adsorbs both soluble barium salts and foreign sulfates so strongly that often both are found in the same precipitate, the relative amounts of each depending upon the manner of precipitation. The higher the concentration of the foreign substance, the greater is the amount of coprecipitation, so that in the ordinary method of precipitation, solutions as dilute as are practically possible are used in the analysis to minimize contamination. Since the precipitation must be made in hot solution in most cases to obtain a sufficiently coarse precipitate to be readily filterable, the possible effect of varying the temperature is not of much importance in studying the conditions of precipitation, and not many data have been gathered on this point.

In agreement with the general rules of coprecipitation (p. 121), the carrying down of foreign anions is greater when the sulfate solution is added to the barium solution than when the precipitation is made in the reverse way; and the opposite holds true for the cation coprecipitation. As already indicated, both foreign anions and cations are likely to be found in the same precipitate; but again in accord with the coprecipitation theory, cation coprecipitation predominates over anion coprecipitation when barium solution is added to sulfate solution and conversely, especially if the solutions are dilute and the mixing is slow and thorough, but exceptions can occur when the specific adsorbabilities of the foreign cation and anion are quite different. The simultaneous addition of a barium salt and a sulfate solution to a dilute hydrochloric acid solution (the method of F. L. Hahn)[1] yields a precipitate which is quite impure,[2] and this method of precipitation is not to be recommended. The precipitate thus obtained consists of very large crystals; but this is of no special advantage, because the precipitate obtained by the ordinary method is sufficiently coarse to be readily filterable. The special digestion method of obtaining barium sulfate, in which the precipitation is made in a cold concentrated solution and the mixture is heated in the presence of a low concentration of hydrochloric acid after the dilution, has not been studied sufficiently to enable it to be said whether or not this procedure gives a purer precipitate than the ordinary method, although there are indications[1] that this method may be of value.

---

[1] F. L. Hahn and R. Otto, Z. anorg. allgem. Chem. *126*, 257 (1923).

[2] I. M. Kolthoff and M. J. van Cittert, Z. anal. Chem. *63*, 392 (1923).

The alkali sulfates are strongly coprecipitated with barium sulfate, potassium sulfate appearing to be more strongly carried down than sodium or lithium, although the difference is not very marked. In acid solutions, sulfuric acid or bisulfates are coprecipitated. Increasing the hydrogen-ion concentration tends to result in the displacement of adsorbed cations but increases the sulfuric acid coprecipitation at the same time. On account of its slight solubility, calcium sulfate is coprecipitated more strongly than the alkali sulfates. The divalent metals are all coprecipitated to a greater or lesser extent (Table XLVII). Ferric iron is more strongly carried down than ferrous for reasons that are considered in the next section.

TABLE XLVII. COPRECIPITATION OF METAL SULFATES WITH BARIUM SULFATE[2]

Conditions of precipitation: Volume of solution 350 ml.; 2 ml. of 2 per cent HCl present. Time of precipitation 4 minutes. $BaCl_2$ added to sulfate solution. Time of standing before filtration, 18 hours

METAL SULFATE	MG. OF FOREIGN SULFATE IN 1 G. $BaSO_4$	
	No Chloride Present	5 g. Metal Chloride Present
Na	4.1	8.7
Li	3.7	6.4
K	5.6	6.7
Cu	6.6	8.8
Cd	16.2	20.8
Zn	6.4[a]	6.1[a]
Ni	4.8	7.7
Mn	9.6	14.8
Fe^{II}	5.7[b]	12.5[b]
Mg	1.5	. . . .
Al	5.8	8.5

[a] 5 ml. of 20 per cent HCl.
[b] 6 ml. of 2 per cent HCl.

The extent of coprecipitation of various anions is indicated in Table XLIX. The carrying-down of chloride is troublesome but less serious than the coprecipitation of nitrate and chlorate.

It may be mentioned that after ignition of a contaminated barium sulfate precipitate, a part of the occluded substance can be washed out with water or dilute hydrochloric acid (compare p. 123). Analytically this behavior is not very important because the contaminant cannot be quantitatively removed in this way.

---

[1] V. Njegovan and V. Marjanović, Z. anal. Chem. *73*, 271 (1928); *74*, 191 (1928).

[2] Based on data given by J. Johnston and L. H. Adams, J. Am. Chem. Soc. *33*, 829 (1911).

Attention has been called in a previous chapter to the favorable effect that standing or digestion before filtration has on reducing the amount of coprecipitated substances in barium sulfate (p. 123).

Errors in the ordinary method of determination of sulfate as barium sulfate and their minimization.

By the *ordinary method* we mean here the customary one that is used in precipitating barium sulfate, in which fairly dilute solutions of barium and sulfate are employed and in which one reagent is added directly to the other solution at or near 100°. In discussing, from the analytical standpoint, the errors that may occur, it is advantageous to consider the problem under three heads, depending upon the composition of the solutions.

1. ***Precipitation of barium sulfate by the addition of barium chloride to sulfuric acid in the absence of other cations and anions, and the reverse precipitation.*** This is the simplest case. When a dilute solution of barium chloride is added slowly with stirring to a hot dilute solution of pure sulfuric acid, there is formed a precipitate of barium sulfate which contains appreciable amounts of chloride as barium chloride. When the precipitation is made in the reverse way, the amount of chloride coprecipitated is greater than before. This is clearly shown in Table XLVIII, which contains some of the data obtained by Richards and Parker[1] in a study of the coprecipitation of barium chloride with barium sulfate.

TABLE XLVIII. COPRECIPITATION OF CHLORIDE WITH BARIUM SULFATE[2]

CONDITIONS OF PRECIPITATION	Cl IN 1 G. OF $BaSO_4$
	mg.
1. $BaCl_2$ (vol. *ca.* 20 ml.) added slowly in slight excess to H_2SO_4 (vol. *ca.* 50 ml.) at boiling temperature; $\frac{1}{4}$ ml. strong HCl present	1.2, 1.3
2. As in (1) but with double the required amount of $BaCl_2$	1.2 (avg.)
3. Reverse precipitation: H_2SO_4 to $BaCl_2$	4.6 (avg.)
4. As in (1) except with 10 ml. of strong HCl present	4.7, 4.2
5. As in (1) except with 20 ml. of strong HCl present	9.1, 7.6
6. As in (1) except precipitation made in a solution four times as dilute	0.7, 0.7
7. As in (1) except $BaCl_2$ added very rapidly	1.8, 1.7

It is also found that precipitates formed by either manner of precipitation contain sulfuric acid, the precipitate obtained by addition of barium solution to sulfuric acid containing more than the one formed in the reverse precipitation. The adsorption of sulfuric acid does not preclude the adsorption of barium chloride or conversely. The adsorption of the latter is the result of the adsorption of barium ions. When barium chloride is added to sulfuric acid drop by drop with vigorous stirring, there will be in the neighborhood of the barium sulfate crystals already formed, ions of hydrogen, sulfate, barium, and chloride. The crystals will naturally adsorb barium and sulfate ions and build up their lattices; and since, if the mixing has been well done, there are more sulfate than barium ions in the region of the surface, there will be a greater chance for hydrogen ions than for chloride ions to be dragged to the surface. The ratio of the amounts of sulfuric acid and barium chloride coprecipitated will depend not only upon the relative concentrations of the two substances in the neighborhood of the surfaces of the growing crystals but also upon their relative adsorbabilities. At any rate, the adsorption of both substances is to be anticipated, but the one which is in excess may be expected to be adsorbed and coprecipitated to a larger extent. If the mixing is not thorough, quite the opposite effect may be found.

---

[1] T. W. Richards and H. G. Parker, Z. anorg. Chem. *8*, 413 (1895).

[2] T. W. Richards and H. G. Parker, Z. anorg. Chem. *8*, 419, 420, 421 (1895).

The absolute amounts of barium chloride and sulfuric acid carried down depend upon the concentrations of the reacting solutions and the rate of mixing, as well as the temperature. Slow addition of reagent and thorough stirring during precipitation both aid in decreasing the amount of occlusion.

When a precipitate of barium sulfate containing both sulfuric acid and barium chloride is heated, the two contaminants react to give barium sulfate, and hydrogen chloride escapes. If equivalent amounts of the two substances were originally present, no error would result; but in nearly every case the amounts are quite different, and after the heating some barium chloride will remain if this substance preponderated, or else sulfuric acid will escape, if it was in excess, leaving behind a pure residue of barium sulfate. In the first case it should be noted that high results will be obtained if sulfate is being determined, because barium chloride remains largely unchanged after moderate ignition, whereas in the second case the results will be low, because sulfate is lost. If barium is being determined, the results will be low in the first case because $BaCl_2$ has a lower molecular weight than $BaSO_4$, whereas in the second case there will be no error at all.

In determining sulfuric acid in pure solution, barium chloride should be added to the former solution because the specific adsorbability of barium chloride is greater than that of sulfuric acid. When the precipitation is so made, rather good results are obtained through a compensation of errors. The small amount of barium chloride left in the ignited precipitate approximately compensates the solubility loss. Thus Richards and Parker[1] found that two precipitates of barium sulfate precipitated from pure dilute sulfuric acid with barium chloride, each weighing *ca.* 0.8 g., contained respectively 0.5 and 1.7 mg. of barium chloride after ignition, whereas the solubility losses were respectively 1.1 and 1.7 mg. If results of the highest accuracy are required, it will be necessary to correct the properly ignited barium sulfate for the chloride it contains and at the same time determine the loss due to the solubility of the barium sulfate. The chloride in the precipitate can be determined by fusing the barium sulfate with sodium carbonate, extracting the melt with water, and determining chloride gravimetrically in the extracts by precipitation as silver chloride after acidification with nitric acid,[1] or by drawing a stream of air through a hot sulfuric acid solution of the barium sulfate into a solution of silver nitrate to absorb the hydrogen chloride evolved, finally determining the excess of silver by titration, or else by weighing the precipitated silver chloride.[2] The chloride found is calculated to barium chloride and deducted from the weight of the precipitate. To determine the solubility loss, the filtrate and the washings are simply evaporated to dryness, the residue is taken up in a small volume of water acidified with a little hydrochloric acid, and the precipitate is collected by filtration, washed, and ignited. It will not often be necessary to make these corrections.

---

[1] T. W. Richards and H. G. Parker, *loc. cit.*

It may be mentioned that it is much easier to determine barium than sulfate in pure solution, because in the former case the precipitate can be moistened with sulfuric acid after ignition and reignited after fuming off the excess acid. In this manner any coprecipitated barium chloride is transformed into sulfate, and the same would occur with any other barium salt of a volatile acid, such as nitrate.

2. *Precipitation of barium sulfate in the presence of cations (as chlorides or sulfates).* This is a more complicated case than the preceding because here the barium sulfate can contain barium chloride, foreign metal sulfate or bisulfate, and sulfuric acid, the amounts of these various substances depending on the composition of the original solution, the method of precipitation, and the length of time between precipitation and filtration. Such a precipitate on ignition may lose hydrochloric acid and sulfuric acid, and the residue may contain a foreign sulfate or its decomposition products, and barium chloride as well, if the latter was originally in excess over sulfuric acid or bisulfate.

(1) *In the presence of the alkali metals.* The determination of sulfate in alkali sulfates or of sulfuric acid in the presence of alkali chlorides is important analytically. Allen and Johnston [3] and Johnston and Adams [4] have carefully studied the effects of various factors on the sulfate determination in the presence of the alkalies. As a result of an investigation of the precipitation of sodium sulfate with barium chloride, the former two authors arrived at the following conclusions regarding the occlusion of sodium sulfate by barium sulfate:

1. A decrease in the concentration of sodium sulfate decreases the coprecipitation slightly.

2. Varying the rate of addition of barium chloride has a rather small effect on the amount of coprecipitation, the tendency of rapid addition being to decrease the quantity of sodium sulfate carried down.

3. Adding the sodium sulfate to the barium chloride solution does not decrease the occlusion to any great extent.

4. Increasing the hydrochloric acid concentration slowly decreases the amount of sodium sulfate coprecipitated.

---

[1] T. W. Richards and H. G. Parker, *loc. cit.*

[2] G. A. Hulett and L. H. Duschak, Z. anorg. Chem. *40*, 196 (1904).

[3] E. T. Allen and J. Johnston, J. Am. Chem. Soc. *32*, 588 (1910).

[4] J. Johnston and L. H. Adams, J. Am. Chem. Soc. *33*, 829 (1911).

5. Allowing the precipitated barium sulfate to stand in the supernatant liquid for some time before filtration reduces the amount of occluded sodium sulfate considerably. Digestion of the precipitate with water, barium chloride, or sodium sulfate solution has no marked effect.

6. Sodium chloride increases markedly the amount of coprecipitation of the alkali sulfate. Sodium chloride itself is not coprecipitated.

7. The ignited precipitate contains only traces of chloride, even when the precipitation is made in the presence of as much as 30 g. of sodium chloride; but before ignition considerable amounts of chloride are present.

The same authors investigated also the volatilization of free sulfuric acid from the precipitates (formed in the presence of sodium sulfate in hydrochloric acid solution) on heating and found that:

1. All precipitates formed in acid solution lose sulfuric acid when heated above 500°.

2. The sulfuric acid loss increases with the concentration of acid present during the precipitation up to 0.1 N and then decreases.

3. In the reverse precipitation (sulfate to barium) a precipitate is obtained which loses much less sulfuric acid.

4. The loss of sulfuric acid increases with the concentration of sodium chloride present.

5. The loss of acid is decreased by increasing the rate of addition of barium chloride.

6. Allowing the precipitate to stand in the supernatant liquid decreases the amount of sulfuric acid volatilized on ignition.

In studying the precipitation of barium sulfate from potassium sulfate solutions, Allen and Johnston obtained similar results; the amount of potassium sulfate coprecipitated was found to be about the same as with sodium sulfate, although the volatilization losses were greater in the presence of potassium chloride than in the corresponding case of the sodium salt.

The determination of sulfate in alkali sulfates by slow precipitation with barium chloride in weakly acid solutions gives low results when the precipitate is ignited, because the residue weighed contains alkali sulfate and no appreciable amount of barium chloride to compensate the deficiency in weight due to the former ($Na_2SO_4 < BaSO_4$, $K_2SO_4 < BaSO_4$), to say nothing of the sulfate lost as sulfuric acid by volatilization. With ammonium sulfate the error is usually more serious than with the other alkali sulfates because a precipitate of barium sulfate containing ammonium sulfate loses all of the latter by volatilization on ignition.

It is possible to reduce the error due to the occlusion of the alkali sulfates and sulfuric acid by:

1. Making the precipitation in the reverse way, i.e., adding the alkali sulfate solution to the acidified barium chloride solution. By making the precipitation in this manner the amounts of alkali sulfate and sulfuric acid occluded are decreased, while the amount of barium chloride carried down is increased; and thereby the two errors, opposite in sign, more nearly compensate each other. As a matter of fact the weight of precipitate thus obtained is usually greater than the true value because of the barium chloride in the ignited residue. When the precipitation is made

by addition of barium chloride to sulfate, the amount of alkali sulfate coprecipitated far outweighs the barium chloride occluded. The method of reverse precipitation has been recommended by Popoff and Neuman.[1]

2. Adding the barium chloride solution *rapidly* to the sulfate solution.[2] Rieman and Hagen [3] compared various methods of precipitation of barium sulfate and found that the most accurate results for sulfur in sodium sulfate, especially in the presence of sodium chloride, were obtained when the barium chloride solution was added rapidly to the sulfate solution according to the directions of Hintz and Weber. Although the weight of the ignited precipitate obtained in the Hintz and Weber method is close to the theoretical value, it cannot be inferred that the good results are not due to a compensation of errors. A study of the actual amounts of occluded substances in barium sulfate precipitated by various procedures would be desirable. On the basis of the good results claimed by Rieman and Hagen, rapid precipitation is used in the procedure given on page 340 for the determination of sulfur in a soluble sulfate.

If a very accurate determination of sulfate in the presence of the alkali metals is required, it can be had by applying corrections for solubility, chloride and alkali sulfate in the precipitate, and loss of sulfuric acid on heating — all as described by Allen and Johnston.[4]

(2) *In the presence of the divalent metals* (cf. Table XLVII). Magnesium is only very slightly occluded by barium sulfate. Calcium causes serious errors, as already mentioned, because calcium sulfate is strongly coprecipitated, as is to be expected from its slight solubility.[5]

In many practical cases it is admissible to make the precipitation of barium sulfate in the presence of moderate amounts of ferrous iron or zinc, if the solution be quite strongly diluted.

(3) *In the presence of trivalent metals.* The important trivalent metals encountered are ferric iron, aluminum, and chromium. Ferric iron has a great tendency to be carried down, this being in great part attributable to the hydrolysis of the iron with the formation of a positively charged colloid of basic ferric salt, which is naturally strongly adsorbed by the negatively charged barium sulfate (p. 120). The coprecipitation can be decreased by making the precipitation in the reverse manner and in the presence of a fairly high concentration of hydrochloric acid (but only at the cost of solubility losses of barium sulfate in the latter case). The error can be eliminated only by removing the trivalent iron by double precipitation with an excess of ammonium hydroxide followed by the removal of ammonium salts from the solution. Often quite satisfactory results can be obtained by reducing iron to the ferrous condition by the action of hydroxylamine, metallic zinc, or aluminum, since divalent iron is much less strongly occluded than trivalent iron.

---

[1] S. Popoff and E. W. Neuman, Ind. Eng. Chem., Anal. Ed. *2*, 45 (1930).

[2] E. Hintz and H. Weber, Z. anal. Chem. *45*, 31 (1906).

[3] W. Rieman III and G. Hagen, Ind. Eng. Chem., Anal. Ed. *14*, 150 (1942).

[4] E. T. Allen and J. Johnston, J. Am. Chem. Soc. *32*, 588 (1910); cf. J. Johnston and L. H. Adams, J. Am. Chem. Soc. *33*, 843 (1911).

[5] For a method which gives better results than the usual one in the determination of sulfate in the presence of calcium, see Johnston and Adams, J. Am. Chem. Soc. *33*, 829 (1911).

Aluminum is not particularly strongly carried down by barium sulfate much less so than iron; but a high concentration of the metal is deleterious. Chromic chromium is an undesirable constituent in a solution from which barium sulfate is to be precipitated. On the one hand it is coprecipitated, and on the other it may prevent the complete precipitation of sulfate (complex chromic sulfates). This complex can be transformed into a chromium acetate complex by the addition of an excess of alkali acetate, thus making the sulfate completely precipitable.

3. ***Precipitation of barium sulfate in the presence of foreign anions.*** The coprecipitation of barium chloride has already been discussed. The occlusion of barium nitrate, chlorate, and phosphate is much greater than that of chloride and can lead to very serious analytical errors (cf. Table XLIX). Nitrate and chlorate must be destroyed before the precipitation of barium sulfate is attempted. This can be accomplished very easily by evaporating the sample to dryness two or three times with concentrated hydrochloric acid:

TABLE XLIX. COPRECIPITATION OF ANIONS WITH BARIUM SULFATE[1]

Conditions of precipitation: 40 ml. of 0.1 *M* sodium sulfate solution were added rapidly to 50 ml. of 0.1 *M* solution of the barium salt diluted with 160 ml. of water. Both solutions were near the boiling point when mixed. The precipitate was filtered off after one minute, and analyzed *directly* for the anion in question.

ANION	MOLE ANION COPRECIPITATED PER MOLE $BaSO_4$
NO_3^-	0.0848
NO_2^-	0.0747
ClO_3^-	0.0584
$Fe(CN)_6^{----}$	0.0330
MnO_4^-	0.0285
Cl^-	0.0176
$Fe(CN)_6^{---}$	0.0090
Br^-	0.0083
CN^-	0.0031
CNS^-	0.0022
I^-	0.0006

$$NO_3^- + 3\,Cl^- + 4\,H^+ \rightarrow Cl_2 + NOCl + 2\,H_2O$$
$$ClO_3^- + 5\,Cl^- + 6\,H^+ \rightarrow 3\,Cl_2 + 3\,H_2O.$$

Other anions are less frequently encountered. It may be mentioned that barium sulfate precipitated in acid solution in the presence of chromate is contaminated by barium chromate (barium sulfate and barium chromate form mixed crystals). Determination of sulfate in the presence of molybdate is unsatisfactory.[2]

---

[1] H. B. Weiser and J. L. Sherrick, J. Phys. Chem. *23*, 205 (1919).

[2] D. A. Lambie and W. R. Schoeller, Analyst *65*, 281 (1940).

Empirical corrections in the determination of sulfate.

Since it is difficult to obtain very accurate results in the determination of sulfate by precipitation as barium sulfate, it has been proposed by Winkler[1] (and others) to apply empirical corrections to the result obtained. The corrections are found by precipitating various amounts of sulfate under the same conditions as hold in the determination of the unknown amount of sulfate and recording the deviations from the theoretical value in a table or constructing a graph.[2]

The principal weakness of this method is that the kind and amount of foreign substances present must be the same in the two cases, and the method can therefore be applied conveniently only when a large number of determinations of sulfate are being made on samples of nearly the same composition.

The ignition of barium sulfate.

Barium sulfate when pure is not decomposed when heated in air until a temperature of about 1400° is reached:[3]

$$BaSO_4 \rightarrow BaO + SO_3.$$

The precipitate is however rather easily reduced to sulfide by carbon formed by the charring of the filter paper. This reduction can be avoided by burning off the filter slowly at a low temperature with free access of air. The final ignition of the barium sulfate need not be made at a temperature higher than 800° or 900° (a Tirrill burner is suitable); higher temperatures are best avoided as possibly leading to a partial decomposition when traces of impurities, such as iron, are present.[4]

Other substances determinable as insoluble sulfates.

Sulfur in forms other than sulfate, e.g., sulfide, sulfite, thiosulfate, etc., can be converted to sulfate by appropriate methods and determined by precipitation with barium chloride. As already indicated, barium can be determined by precipitation with a slight excess of sulfuric acid. Strontium can be precipitated quantitatively as the sulfate if alcohol is added to reduce the solubility of the precipitate. Rarely, calcium is precipitated and determined as sulfate in the presence of alcohol. By using a proper excess of sulfuric acid, lead can be separated and determined as the sulfate (p. 699).

---

[1] See for example L. W. Winkler, Z. angew. Chem. *33*, I, 160 (1920).

[2] C. E. Waters, Bur. Standards Tech. Paper No. 177, p. 25.

[3] W. Mosttowitsch, Metallurgie *6*, 450 (1909); Chem. Abst. *5*, 841 (1911).

[4] H. A. Fales and W. S. Thompson, Ind. Eng. Chem., Anal. Ed. *15*, 206 (1939), recommend drying barium sulfate at 110° to 120° instead of igniting.

Determination of sulfur in a soluble sulfate.

The following procedure is designed for the determination of sulfur in the sulfates of the alkali metals. The precipitation is made by rapidly adding barium chloride in slight excess to the hot sulfate solution. Under these conditions the coprecipitation of barium chloride outweighs that of the alkali sulfate, and the ignited precipitate is usually heavier than the theoretical weight by a few parts per thousand.[1] The special advantage of this method of precipitation is the relatively slight effect of the presence of a fair amount of alkali chloride which may be introduced in the preparation of the sample.

Small amounts of ferrous iron, magnesium, zinc, and aluminum may be present. Calcium and ferric iron should not be present in appreciable amounts. Strongly coprecipitable anions (nitrate, chlorate, etc.) must be absent.

As already mentioned (p. 334), good results can be obtained in the determination of sulfate in sulfuric acid solutions containing no alkali metals by adding the barium chloride solution slowly. This method of precipitation may be applied in the determination of sulfur in pyrite (p. 342).

Procedure. Weigh out a sufficient amount of sample to contain approximately 0.1 g. of sulfur into a 600 ml. beaker provided with a stirring rod, add 25–50 ml. of water, and stir to dissolve.[2] Acidify with 2 ml. of concentrated hydrochloric acid and dilute to 350 or 400 ml. with water. Dilute 20 ml. of 5 per cent barium chloride (5 g. $BaCl_2 \cdot 2\,H_2O$ in 100 ml. of solution — *ca.* 0.2 M) to 75 or 100 ml. in a small beaker, heat nearly to boiling, and add the solution rapidly (over a period of about 5 seconds) with stirring to the sulfate solution, which has been heated to near the boiling point. Allow the precipitate to settle, and test the supernatant liquid for complete precipitation by adding a little barium chloride solution. If a precipitate should form, add more barium chloride, allow the precipitate to settle as before, and test again. When an excess of precipitant has been added, set the covered beaker aside for an hour or two on the steam bath (or over a low-temperature hot plate or a low flame, so adjusted that the solution does not boil). If convenient allow the solution to stand on the steam bath overnight.

---

[1] If the precipitation is made by adding the barium chloride solution slowly to the sulfate solution, the results are usually low to the extent of a few parts per thousand owing to the occlusion of alkali metal sulfate or sulfuric acid; but this error becomes larger if alkali metal chlorides are present.

[2] If the sample is insoluble in water, add hydrochloric acid dropwise with warming until it is dissolved. Then add 2 ml. of the concentrated acid in excess. If sulfuric acid is analyzed, omit the hydrochloric acid.

After digestion, decant the clear supernatant liquid through a fine-grained ashless filter paper (p. 250), receiving the filtrate in a clean beaker. For safety, test the first portions of the filtrate for complete precipitation by adding a few drops of barium chloride solution. When most of the supernatant liquid has been poured through the filter and while nearly all of the precipitate still remains in the precipitation beaker, empty the beaker containing the filtrate, and then replace it beneath the funnel. Now transfer the precipitate to the paper with a jet of water from the wash bottle (p. 253). If any of the precipitate runs through the paper (it should not if a fine paper is used), pour the filtrate through the paper, and repeat if necessary until the solution runs through perfectly clear. Use a policeman to remove any precipitate adhering to the walls of the beaker or to the stirring rod, finally examining the vessel carefully to see that all barium sulfate has been removed. Wash the precipitate and paper 8 or 10 times with small portions of warm water, proceeding as directed on p. 257. Test the last few milliliters of washings with a drop or two of silver nitrate solution for the presence of chloride, this ion being indicative of incomplete washing. If a positive test is obtained, continue the washing until no test, or at the most only a very faint opalescence, is given.

Fold the moist paper around the precipitate and place in a weighed porcelain crucible previously ignited to redness and cooled in a desiccator. Dry the paper by heating the loosely covered crucible placed in a triangle some centimeters above a small flame (p. 259). Then gradually increase the heat until the paper chars and volatile matter is expelled. Do not heat to redness at this stage, and do not let the paper burst into flame. When the charring is complete, raise the temperature of the crucible to low redness, and burn off the carbon with free access of air (crucible slightly inclined and with cover displaced). When the carbon is gone, ignite for 10 to 15 minutes at moderate redness over a Tirrill burner. Then allow the crucible to cool somewhat in the air, and place it in the desiccator to cool to room temperature. Weigh, and repeat the ignition with 10-minute periods of heating until constant weight (± 0.2 mg.) is attained.

Report the percentage of S, SO_3, or SO_4 in the sample as required.

Note:

If desired, a Gooch or porous porcelain filter crucible may be used to collect the precipitate. In this case the ignition (also of the empty crucible) is conveniently made in a muffle at 900° or as described on p. 261.

Determination of sulfur in a sulfide.

The determination of sulfur in the naturally occurring sulfides of iron, copper, arsenic, etc., is generally based on the oxidation of sulfide to sulfate and the precipitation of the latter as barium sulfate. Two general methods are in common use for the decomposition of insoluble sulfides, viz.:

1. Oxidation in the wet way by such reagents as aqua regia, fuming nitric acid, and bromine with nitric or hydrochloric acid. For example, the action of bromine and nitric acid on pyrite ("iron pyrites") may be represented as follows:

$$FeS_2 + 15\,Br + 3\,HNO_3 + 8\,H_2O \rightarrow Fe(NO_3)_3 + 2\,H_2SO_4 + 15\,HBr.$$

2. Fusion with an alkaline oxidizing agent such as sodium peroxide or a mixture of sodium carbonate and potassium nitrate:

$$2\,FeS_2 + 15\,Na_2O_2 \rightarrow 4\,Na_2SO_4 + Fe_2O_3 + 11\,Na_2O.$$

Each method has its advantages and disadvantages. Fusion with sodium peroxide is a very effective method of decomposing refractory sulfides; but there are a number of objections to its use in accurate work, one of which is the introduction of a large amount of sodium. Oxidation in the wet way is free from this objection, but the action is slower, and greater care must be taken to obtain complete decomposition; moreover, the nitric acid introduced must be destroyed by evaporation with hydrochloric acid, and the iron brought into solution must be removed or reduced to the ferrous condition to prevent serious contamination of the barium sulfate. It should be noted that when the wet attack is used sulfur present as an insoluble sulfate (e.g., barium or lead sulfate) largely escapes determination. For siliceous materials (rocks) containing very small amounts of sulfur (as sulfide, sulfate, or both), fusion with a 10 : 1 mixture of sodium carbonate and potassium nitrate is suitable. This fusion may be made in a platinum crucible since the metal is not seriously attacked by this flux. The introduction of alkali salts is of relatively small importance here, because the amount of sulfur present is very small, i.e., the coprecipitation of even a few per cent of alkali sulfate is hardly of moment when the sulfur content of the sample is, let us say, 0.1 per cent. Sulfides soluble in nonoxidizing acids may be analyzed by collecting the hydrogen sulfide evolved on treatment with acid in a suitable medium and determining the sulfur therein gravimetrically or volumetrically (see the determination of sulfur in steel, p. 719).

Attention must be called to the danger of contamination in the decomposition of sulfides when gas flames are used for heating. The products of combustion of gas contain the oxides of sulfur, and these are taken up avidly by alkaline fluxes and also by solutions. The error from this source will generally be small if care is taken to exclude the flame gases. Electrical heating is to be preferred. In the determination of small amounts of sulfur it is of the greatest importance to run blanks simultaneously with the determination itself to correct for sulfur introduced from the atmosphere and in the reagents. It should also be mentioned that in preparing a sulfide for analysis, the sample should not be ground unduly fine on account of danger of oxidation of sulfide to sulfur dioxide.[1]

As an example of the determination of sulfur in a sulfide we have chosen the analysis of pyrite. The determination of sulfur in this material is of great commercial importance, since it furnishes a valuable source of sulfur compounds (sulfur dioxide, sulfuric acid). In the following procedure the interference due to iron is minimized by reducing it to the ferrous state and making the precipitation in a cold dilute solution.

Procedure.[2] Weigh 0.5. g. of pyrite,[3] ground to pass an 80-mesh sieve, into a dry 250 ml. covered beaker, and add 6 to 8 ml. of a mixture of 2 parts by volume of bromine to 3 parts of carbon tetrachloride (hood !). Allow the mixture to stand for 15 minutes at room temperature with occasional shaking; then add 10 ml. of concentrated nitric acid and let stand again for 15 minutes with occasional agitation. Next heat below 100° by placing the beaker on a thick asbestos board over the steam bath until all action has ceased and most of the bromine has been expelled. Then raise the cover glass and evaporate to dryness by heating directly on the steam bath. Add 10 ml. of concentrated hydrochloric acid, mix, evaporate to dryness, and bake the residue for 30 to 60 minutes at 100° to dehydrate the silica. To the residue add 1 to 2 ml. of hydrochloric acid and then, after a few minutes, 50 ml. of water. Rinse down the sides of the beaker as well as the cover glass. Heat to boiling and keep at this temperature for about 5 minutes. Allow to cool for 5 minutes, and then add 0.2 g. of pure powdered aluminum to reduce the iron. Stir until the solution becomes colorless, allow to cool somewhat, and then wash down the sides of the beaker and the cover glass. Filter off insoluble matter on a small filter, and catch the filtrate in a liter beaker. Wash the residue and the paper thoroughly with hot water. Dilute the filtrate and washings to 700 ml., and add 2 ml. of concentrated hydrochloric acid. Precipitate the sulfate in the cold by adding 50 ml. of 5 per cent barium chloride solution dropwise, with stirring, at a rate not exceeding 5 ml. per minute. Allow the precipitate to settle for 2 hours or, better, overnight. Filter, using paper or a Gooch crucible, and wash the precipitate as described on p. 341. Ignite the precipitate to constant weight (p. 341). Report the percentage of sulfur found. In the most accurate work, run a blank through all the steps of the procedure.

PROBLEMS

1. If 0.5500 g. of a soluble sulfate yielded 0.6460 g. of barium sulfate, what was the percentage of sulfur in the sample?

---

[1] E. T. Allen and J. Johnston, J. Ind. Eng. Chem. *2*, 196 (1910).

[2] W. S. Allen and H. B. Bishop, 8th Int. Congr. Appl. Chem. 1–2 (I–II), 48, 1912; J. Ind. Eng. Chem. *11*, 46 (1919).

[3] If the percentage of sulfur is to be reported on the dry basis (p. 240), determine hygroscopic water in a separate 1 g. portion of sample.

2. Calculate the volume of 0.2 *M* barium chloride solution required to precipitate the sulfate in 0.5 g. of sodium sulfate. What weight of barium sulfate will be obtained? *Ans.* 17.60 ml.; 0.8216 g.

3. It is desired to prepare a solution of barium chloride of such strength that 1 ml. shall represent 1.00 mg. of SO_4. What weight of $BaCl_2 \cdot 2\,H_2O$ must a liter of such a solution contain? *Ans.* 2.543 g.

4. From the following data obtain the formula of a sulfide mineral:
1.000 g. yielded 0.3451 g. of copper
0.5000 g. contained 0.1525 g. of iron
0.3000 g. yielded 0.7640 g. of barium sulfate.

5. It is desired that each mg. of ignited barium sulfate residue shall represent 0.10 per cent of sulfur. What weight of sample must be taken? *Ans.* 0.137 g.

6. Calculate the weight of an unignited braium sulfate precipitate obtained from 0.1000 g. of SO_4 when the precipitate contains (a) 1 per cent of Na_2SO_4, (b) 1 per cent K_2SO_4, (c) 1 per cent $(NH_4)_2SO_4$, (d) 1 per cent $BaCl_2$, (e) 1 per cent $Fe_2(SO_4)_3$, (f) 1 per cent $KHSO_4$, (g) 1 per cent $KHSO_4$ + 1 per cent $BaCl_2$. What will be the weights of these ignited precipitates if the ignition is made at 600°? What are the relative errors in percentage of SO_4 in each case as calculated from the weights of the ignited residues?

7. A solution of barium and lead is treated with sufficient ammonium acetate to keep lead sulfate in solution, and then an excess of ammonium sulfate is added. Is it to be expected that the precipitated barium sulfate will be free from lead?

8. The sulfate content of a ferric sulfate solution is determined by adding an excess of carbonate-free ammonium hydroxide followed by an excess of barium chloride solution; the mixture is acidified and the barium sulfate filtered off. What is the function of the ammonium hydroxide? What substance or substances are likely to be carried down by barium sulfate precipitated in ammoniacal solution? Will the results be high or low?

CHAPTER XXI

DETERMINATION OF CALCIUM

Method.

Calcium is precipitated as calcium oxalate by treating a hot hydrochloric acid solution with ammonium oxalate or oxalic acid and neutralizing with ammonium hydroxide:

$$Ca^{++} + C_2O_4^{=} + H_2O \rightarrow CaC_2O_4 \cdot H_2O.$$

The precipitate is washed with dilute ammonium oxalate solution, ignited to calcium carbonate or oxide by heating to the proper temperature or converted into calcium sulfate by treatment with sulfuric acid, and weighed in any of these forms.[1] Cations other than the alkalies and magnesium must be absent.

Solubility of calcium oxalate.

One liter of water dissolves 6.7 mg. of calcium oxalate monohydrate [2] at 25° and 14.0 mg. at 95°. In neutral solutions containing ammonium oxalate the solubility is, of course, much less, and a dilute solution of this salt is therefore used to wash the precipitate in the gravimetric determination of calcium.

The solubility of calcium oxalate increases with increasing hydrogen-ion concentration, as a consequence of the removal of oxalate ions from the system CaC_2O_4 (solid) $\rightleftarrows Ca^{++} + C_2O_4^{=}$. Oxalate ions are transformed into bioxalate ions and at higher acidities into oxalic acid. From the equilibria:

$$C_2O_4^{=} + H^+ \rightleftarrows HC_2O_4^{-} \qquad K_2 = 6 \times 10^{-5}$$
$$HC_2O_4^{-} + H^+ \rightleftarrows H_2C_2O_4 \qquad K_1 = 6.5 \times 10^{-2}$$

---

[1] Calcium oxalate monohydrate is also a weighing form for calcium but not a desirable one.

[2] Three hydrates of calcium oxalate are known, viz., $CaC_2O_4 \cdot H_2O$, $CaC_2O_4 \cdot 2\,H_2O$, and $CaC_2O_4 \cdot 3\,H_2O$. Of these, the monohydrate is the stable form under ordinary conditions and is always obtained when the precipitation is made in hot solution. The di- and trihydrate, which are formed by precipitation in cold solution under special conditions, are transformed into the monohydrate on standing in the liquid, especially rapidly at higher temperatures.

it is seen that as a monobasic acid oxalic acid is fairly strong, but as a dibasic acid it is a typically weak acid. It is a relatively simple matter to calculate the solubility of calcium oxalate at a given pH.

Suppose it is required to find the solubility at pH = 4.

In a saturated solution of calcium oxalate the following relation holds:

$$[Ca^{++}] = [C_2O_4^{=}] + [HC_2O_4^{-}]. \tag{1}$$

Furthermore,

$$\frac{[H^+][C_2O_4^{=}]}{[HC_2O_4^{-}]} = K_2 = 6 \times 10^{-5}. \tag{2}$$

At

$$[H^+] = 10^{-4},\ [HC_2O_4^{-}] = 1.7\,[C_2O_4^{=}]. \tag{3}$$

From (1) and (3) it is found that

$$[Ca^{++}] = 2.7\,[C_2O_4^{=}]. \tag{4}$$

Moreover,

$$[Ca^{++}][C_2O_4^{=}] = S_{CaC_2O_4 \cdot H_2O} = 2 \times 10^{-9}\ (25^\circ). \tag{5}$$

Combining (4) and (5),

$$[Ca^{++}]^2 = 2.7\,S_{CaC_2O_4 \cdot H_2O} \tag{6}$$

$$\therefore\ [Ca^{++}] = 1.6\sqrt{S_{CaC_2O_4 \cdot H_2O}} = 7 \times 10^{-5}.$$

Since $\sqrt{S_{CaC_2O_4 \cdot H_2O}}$ represents the solubility of calcium oxalate in pure water (pH = 7), it is found that increasing the acidity of the solution to pH = 4 increases the solubility of the precipitate only 1.6 times.

In any actual determination of calcium an excess of oxalate is used in the precipitation, and the solubility is thereby greatly decreased. Suppose that the excess of oxalate in the solution after precipitation corresponds to a concentration of 0.1 *M*. Then

$$[C_2O_4^{=}] + [HC_2O_4^{-}] = 10^{-1}. \tag{7}$$

From (2) and (7), remembering that $[H^+] = 10^{-4}$, it follows that

$$[C_2O_4^{=}] = 3.8 \times 10^{-2}.$$

Accordingly, the solubility of calcium oxalate in a medium having a pH of 4 and 0.1 *M* in oxalate is:

$$[Ca^{++}] = \frac{S_{CaC_2O_4 \cdot H_2O}}{3.8 \times 10^{-2}} = 5 \times 10^{-8}.$$

This value is equivalent to 7×10^{-6} g. or 0.007 mg. of $CaC_2O_4 \cdot H_2O$ per liter.

From the above it may be inferred that calcium is quantitatively precipitated at a pH of 4. This has also been shown experimentally. Even from dilute acetic acid medium calcium is precipitated quantitatively. However, when the solution contains even relatively small amounts of a strong acid, such as hydrochloric acid, the precipitation is no longer quantitative.

The presence of magnesium increases the solubility of calcium oxalate very appreciably as a consequence of the formation of a complex magnesium oxalate which withdraws oxalate ions. The effect is counteracted by the addition of an excess of oxalate.

When magnesium is present in solution with calcium, care must be taken to add enough oxalate to transform magnesium into the complex oxalate, or serious solubility losses of calcium may ensue.

Precipitation of calcium oxalate.

Precipitation of calcium from cold neutral or ammoniacal solutions gives an extremely finely divided precipitate which can be filtered and washed only with difficulty. Therefore the precipitate is never formed in cold solution (except as noted below). Formerly it was the practice to make the precipitation by adding oxalate to a hot neutral or ammoniacal calcium solution. The precipitate thus obtained is coarse-grained enough to be filtered without any particular difficulty. It is much better, however, to precipitate calcium oxalate by adding ammonium oxalate to a hot *acid* solution of the calcium salt and finally neutralizing with ammonium hydroxide. Depending upon the acidity, more or less of the calcium oxalate will be precipitated on the addition of the oxalate. This precipitate will be very coarse on account of the low supersaturation of the solution with respect to calcium oxalate. The remainder of the calcium is also thrown down in the form of relatively large crystals if the acid is neutralized by the moderately slow addition of ammonium hydroxide to the hot solution. The precipitate thus obtained can be filtered and washed with the greatest ease.[1]

The precipitate thus formed by the neutralization of an acid solution may be contaminated to a slight extent with coprecipitated oxalic acid or acid oxalate, but this does not matter if the precipitate is ignited to oxide or carbonate, or converted into sulfate and weighed as such. It is also found that this method of precipitation gives satisfactory, although slightly high, results when calcium is determined volumetrically with potassium permanganate (p. 605). In the permanganimetric method the oxalate precipitate is dissolved in hot sulfuric acid, and the liberated oxalic acid is then titrated with standard permanganate solution. The volumetric method can give accurate results only when the ratio of $C_2O_4^=$ to Ca^{++} in the precipitate is 1 : 1. The precipitate formed in acid solutions in the way mentioned has a composition which closely approaches this ratio. However, a precipitate obtained by adding ammonium oxalate to a neutral or ammoniacal solution is contaminated with basic calcium oxalate, and decidedly low results are then obtained in the permanganimetric method.[2]

---

[1] H. H. Willard and F. L. Chan (Willard and Furman, *Elementary Quantitative Analysis*) neutralize a strongly acid solution of calcium, containing excess oxalate, by adding much urea and heating just below the boiling point. The urea is thus slowly hydrolyzed:

$$(NH_2)_2CO + H_2O \rightarrow CO_2 + 2\ NH_3$$

and extremely coarse crystals of calcium oxalate are formed as a result of the slow neutralization. The neutralization requires from twenty to sixty minutes for completion.

[2] Unpublished data of the authors.

Interfering substances.

The determination of calcium by precipitation as oxalate, in the manner described, requires the absence of elements that form slightly soluble oxalates or which are otherwise precipitated under the conditions of the determination. By virtue of this requirement, calcium must first be separated from virtually all metals save the alkalies and magnesium before the oxalate precipitation can be made.[1] When *small* amounts (a few milligrams) of barium are present, double or triple precipitations of calcium oxalate suffice to separate the two elements.

In the general case it is necessary to precipitate calcium oxalate from a solution containing magnesium and the alkali metals. The coprecipitation of these cations as well as certain anions must therefore be taken into account. The subject of the contamination of the calcium oxalate precipitate by magnesium is a peculiarly complex one, and a consideration of this important matter is reserved for special treatment in a later section of this chapter.

Calcium oxalate displays a distinct tendency to carry down the alkali metals. These cations are carried down as the oxalates. In the usual gravimetric method in which the precipitate is finally weighed as calcium oxide, carbonate, or sulfate, the possible presence of sodium and potassium must be borne in mind, and in the volumetric method (titration with permanganate) that of ammonium as well. It will be seen from Table L that sodium is much more strongly coprecipitated than potassium. Unless inordinately large amounts of potassium are present, the quantity of this cation carried down by the precipitate is so small that a double precipitation is not required in ordinary analytical work. The presence of sodium calls for a double precipitation of calcium oxalate. Precipitation from ammoniacal solution yields a precipitate containing less sodium (and potassium) than one formed by slowly neutralizing an acid solution with ammonium hydroxide. It is to be noted that calcium oxalate precipitated with ammonium oxalate contains appreciable amounts of ammonium oxalate.

The "digestion method" of precipitation described on p. 125 can be applied with advantage in obtaining a fairly pure precipitate of calcium oxalate in the presence of sodium. In this method ammonium oxalate is added rapidly to the neutral calcium solution at room temperature. The mixture is then diluted, preferably acidified with acetic acid, and heated on the steam bath from twelve to twenty-four hours. The digestion results in the conversion of the higher hydrates of calcium oxalate, which have been precipitated in the cold solution, into the monohydrate; and the slow recrystallization thus effected eliminates the greater part of the coprecipitated sodium or ammonium. Under the proper conditions the amount of sodium in the precipitate is reduced to such an extent that a double precipitation is not necessary in many cases.

---

[1] When strontium is present it is precipitated as the oxalate with calcium and is separated later by dissolving the ignited precipitate in nitric acid, rendering the nitrates anhydrous and extracting with absolute alcohol-ether. Strontium nitrate is insoluble in this mixture, whereas calcium nitrate is freely soluble.

TABLE L. COPRECIPITATION OF ALKALIES WITH CALCIUM OXALATE [1]

(0.1 g. of calcium as chloride used in each determination)

CONDITIONS OF PRECIPITATION	PERCENTAGE OF ALKALI OXALATE IN $CaC_2O_4 \cdot H_2O$
SODIUM (1.7 g. sodium chloride present in each case)	
1. 50 ml. of 2% ammonium oxalate solution added to 250 ml. of calcium solution containing 5 ml. of concentrated hydrochloric acid; neutralization made with dilute ammonia added dropwise to hot solution. Precipitate filtered after several hours	1.3
2. 50 ml. of 2% ammonium oxalate added slowly to ammoniacal (1 ml. concentrated ammonia) solution having volume of 250 ml., at boiling temperature	0.8
3. 25 ml. of 4% ammonium oxalate added at one stroke to cold neutral calcium solution having volume of 250 ml. Precipitate digested in mother liquor at 100° for 2 days	0.2
POTASSIUM (1.5 g. potassium chloride present in each case)	
1. 50 ml. of 2% ammonium oxalate solution added to 200 ml. of hot calcium solution containing 2 ml. of concentrated hydrochloric acid; dilute ammonia then added slowly to neutralization	0.1 to 0.2
2. 50 ml. 2% ammonium oxalate solution added to 200 ml. of hot ammoniacal (1 ml. concentrated ammonia) calcium solution	0.03
AMMONIUM	
1. 50 ml. of 2% ammonium oxalate added to 200 ml. of hot calcium solution containing 2 ml. of concentrated hydrochloric acid (no added ammonium chloride); then neutralized with dilute ammonia	0.2 to 0.3
2. 50 ml. of 2% ammonium oxalate added to 200 ml. of hot ammoniacal (1 ml. concentrated ammonia) calcium solution	0.2 to 0.3
3. As in (1) except 1 g. of ammonium chloride present	0.3 to 0.4

---

[1] I. M. Kolthoff and E. B. Sandell, J. Phys. Chem. 37, 448 (1932).

Sulfate is quite strongly coprecipitated with calcium oxalate, owing to the low solubility of calcium sulfate. The presence of sulfate in the precipitate leads to high results when calcium carbonate is used as the weighing form and possibly also when the precipitate is ignited to the oxide, although in the latter case more or less of the calcium sulfate is decomposed into the oxide at the high temperature of the ignition. Of course, there is no error if the precipitate is converted into calcium sulfate and weighed as such. In the permanganimetric method the results for calcium are low in the presence of sulfates, unless there are compensating errors. Phosphate and arsenate are not coprecipitated to any marked extent if the precipitation of calcium is made in acid solution, i.e., if the acid solution containing excess oxalate is slowly neutralized with ammonium hydroxide.[1] Other anions less frequently encountered, such as iodate and chromate, are carried down by calcium oxalate, and double precipitations are required when they are present. The halides are coprecipitated in extremely small amounts, usually not more than a few hundredths of a per cent. It may be noted that the coprecipitation of the anions is greater in hot solutions than in cold, the reverse being true for the cations.

Modified oxalate method. Instead of making the solution finally ammoniacal in the precipitation of calcium oxalate, it is sometimes advantageous to keep it slightly acid. When this is done, calcium can be precipitated in the presence of iron, titanium, and other metals. In this method [2] the hot hydrochloric acid solution containing at least 1 per cent of ammonium oxalate monohydrate is treated with ammonium hydroxide until the pH is 3–4 (light green color with bromphenol blue). The mixture is digested at 100° for one or two hours, and the precipitate is washed with a solution containing ammonium oxalate and oxalic acid (2 g. and 1 g. respectively per liter). Double precipitations should be made. The method may be used for the determination of calcium in phosphate rock.

Weighing forms of calcium.

The following weighing forms of calcium have been proposed: $CaC_2O_4 \cdot H_2O$, CaC_2O_4, $CaCO_3$, CaO, $CaSO_4$, and CaF_2. The first four forms are obtained by heating the precipitate of calcium oxalate at suitable temperatures, and the last two by treating the precipitate, or its ignition products, with sulfuric and hydrofluoric acids respectively. Of these, the carbonate, oxide, and sulfate are well-established weighing forms that have long been used.

Calcium oxalate monohydrate. In recent years a number of workers [3] have recommended weighing calcium as $CaC_2O_4 \cdot H_2O$. It is stated that the monohydrate is stable at 100° to 115° and can be dried by heating in this temperature range for one or two hours.[1] At first sight, calcium oxalate monohydrate appears to be an attractive weighing form for the element. However, the authors have investigated the suitability of this weighing form and have come to the conclusion that it cannot be recommended for accurate work. In the first place, calcium oxalate monohydrate as ordinarily precipitated, whether formed in acid or ammoniacal solution, always contains foreign water which is not expelled on long-continued heating at 100° to 120°. Moreover, the precipitate thus dried is hygroscopic. It was found that calcium oxalate monohydrate free from coprecipitated water could be obtained by applying the digestion method of precipitation as described on p. 125. Unfortunately, the monohydrate is not perfectly stable at temperatures of 100° and above; there is the danger that it may be converted partially into the anhydrous oxalate. In an atmosphere of relatively high humidity the monohydrate appears to be stable up to 120°, but in very dry air it may begin to decompose at 110° or even lower. The manner of precipitation affects the stability of the monohydrate. Precipitates formed in slightly acid solution are more stable than those formed in ammoniacal or neutral solutions.

---

[1] However, if magnesium is simultaneously present, magnesium ammonium phosphate or arsenate is precipitated to a greater or lesser extent depending upon the final pH of the solution.

[2] J. I. Hoffman and G. E. F. Lundell, J. Research Natl. Bur. Standards *20*, 607 (1938); H. D. Chapman, Soil Science *26*, 479 (1928).

[3] See, for example, S. Goy, Chem. Ztg. *37*, 1337 (1913); L. W. Winkler, Z. angew. Chem. *31*, 187 (1918); O. Brunck, Z. anal. Chem. *94*, 81 (1933); H. Sibelius, Suomen Kemistilehti A. *8*, 25 (1935).

In addition, this weighing form suffers from the disadvantage that coprecipitated ammonium oxalate is not eliminated in the heating and is weighed with the calcium oxalate. For these reasons weighing the precipitate as calcium oxalate monohydrate can only be recommended for small amounts of calcium. If the monohydrate is used as a weighing form, it should be dried at 105° to 110°, not higher. The results will be high to the extent of 0.5 to 1.0 per cent under the usual conditions.[2]

At temperatures in the neighborhood of 200° calcium oxalate monohydrate loses its water of crystallization, yielding the anhydrous oxalate, which has also been recommended as a weighing form. Anhydrous calcium oxalate is so hygroscopic, however, that it is not suitable for the purpose.

Calcium carbonate. Above 350° calcium oxalate begins to decompose into calcium carbonate:

$$CaC_2O_4 \rightarrow CaCO_3 + CO.$$

At 475° the decomposition is rapid. Now it must be taken into consideration that calcium carbonate itself decomposes at high temperatures:

$$CaCO_3 \rightleftarrows CaO + CO_2.$$

At any given temperature a mixture of calcium carbonate, calcium oxide, and carbon dioxide in equilibrium with one another exerts a certain definite carbon dioxide pressure. If the partial pressure of carbon dioxide in the atmosphere adjacent to the mixture of oxide and carbonate is greater than the equilibrium pressure for that temperature, the above reaction will run from right to left; and given a sufficient time, the oxide will be completely converted into the carbonate, provided the pressure of the carbon dioxide is maintained above the equilibrium pressure. Conversely, calcium carbonate can never be decomposed into the oxide so long as the pressure of carbon dioxide in the surrounding gas phase is greater than the equilibrium pressure of the system $CaCO_3$—CaO—CO_2 at the temperature of heating. On the basis of these properties of the system, it is possible to predict the temperature at which calcium carbonate will decompose when heated in the air. It is necessary to know only the dissociation pressure of calcium carbonate at various temperatures and the carbon dioxide content of the atmosphere. Dissociation pressures of calcium carbonate are given in Table LI. Atmospheric air normally contains 0.03 per cent of carbon dioxide by volume. When the atmospheric pressure is 760 mm., this value corresponds to a partial pressure of carbon dioxide equal to 760×0.0003, or 0.228 mm. of mercury. In atmospheric air, then, calcium carbonate will be perfectly stable as long as its decomposition pressure does not exceed 0.228 mm. Referring to Table LI, we find tnat the dissociation pressure of the carbonate does not reach this limiting value until a temperature slightly above 500° is reached. Above this limiting temperature it is to be expected that calcium carbonate will begin to decompose, if there is no delayed transformation or other complicating factors.

---

[1] J. Dick, Z. anal. Chem. *77*, 358 (1929), recommends washing the precipitate successively with water, alcohol, and ether, and then drying briefly in the air or in a vacuum desiccator at room temperature. L. Moser and L. von Zombory, Z. anal. Chem. *81*, 95 (1930), have raised objections to this procedure.

[2] If calcium oxalate monohydrate is precipitated slowly by heating the acid solution with urea (p. 347), crystals of macro size are obtained, which can be weighed air-dry after washing with acetone. The results are close to the theoretical under specified conditions. See E. B. Sandell and I. M. Kolthoff, Ind. Eng. Chem., Anal. Ed. *11*, 90 (1939).

TABLE LI. DISSOCIATION PRESSURES OF CALCIUM CARBONATE [1]

TEMPERATURE	PRESSURE OF CO_2 (MM. OF MERCURY)
20°	2.2×10^{-20}
200°	7.8×10^{-9}
400°	0.3×10^{-3}
500°	0.15
600°	2.98
700°	31.2
800°	208
882°	760
900°	984

---

[1] L. Andrussow, Z. physik. Chem. *116*, 95 (1925). It should be mentioned that the dissociation pressures of calcium carbonate depend somewhat upon such factors as particle size, the degree of perfection of the crystals, and the presence of traces of impurities.

Willard and Boldyreff[1] have studied the suitability of calcium carbonate as a weighing form for calcium. They found that for the complete decomposition of calcium oxalate into carbonate in a reasonable period of time the temperature must be at least 450°. These authors further found that above 550° calcium carbonate loses carbon dioxide. When calcium is to be weighed as the carbonate, the oxalate precipitate should be ignited in the temperature range 475° to 525°. Since the temperature must be controlled within rather narrow limits, an electric furnace provided with a pyrometer or a suitable thermometer must be used. If such equipment is available, it is recommended that calcium be weighed as the carbonate for the most accurate results. The precipitate must then be collected in a Gooch or porcelain filter crucible and not in paper, because the latter gives an ignited residue containing carbon.

In the old method of determining calcium as carbonate, the oxalate precipitate was ignited at low redness by means of a burner; the residue was moistened with ammonium carbonate solution to convert any oxide formed into carbonate, briefly ignited, and then weighed. The procedure was repeated until constant weight was attained. This method is not to be recommended.

If the precipitate is heated in a stream of carbon dioxide, the temperature may be raised to 850° without fear of decomposing the carbonate. This method gives good results[2] but is not a very convenient one.

Calcium oxide. At approximately 880° the dissociation pressure of calcium carbonate is 760 mm. This means that at temperatures very slightly above this value, calcium carbonate can be converted completely into the oxide even when surrounded by an atmosphere of carbon dioxide at atmospheric pressure. Therefore by heating calcium carbonate even in a closely covered crucible to this temperature, it may be expected that the carbonate will be converted quantitatively into the oxide in spite of the fact that the carbon dioxide is not allowed to escape freely, as long as the pressure within the crucible is that of the atmosphere. However, on cooling there would be a recombination of calcium oxide and carbon dioxide with the result that some calcium carbonate would be formed. Actually the ignition is made in a loosely covered crucible so that the carbon dioxide escapes by diffusion and convection, being replaced by air. In this manner the partial pressure of carbon dioxide is kept far below the atmospheric pressure, and there is not enough of the gas left in the crucible at the end to form any significant amount of calcium carbonate. It is found, however, that the rate of decomposition of calcium carbonate is so slow in the neighborhood of 900° that it is advantageous practically to make the ignition at a higher temperature, say in the range 1100° to 1200°. Moderate amounts of calcium carbonate can be quantitatively converted into the oxide in a relatively short time by ignition in a platinum crucible over a blast lamp or a Meker burner. The ignition cannot be successfully made in a porcelain crucible under these conditions, and an electrically heated muffle furnace must then be used.

---

[1] H. H. Willard and A. W. Boldyreff, J. Am. Chem. Soc. *52*, 1888 (1930).

[2] H. W. Foote and W. M. Bradley, J. Am. Chem. Soc. *48*, 676 (1926).

Due care must be taken in cooling and weighing the ignited residue of calcium oxide, because it avidly takes on water and, moreover, slowly reacts with the carbon dioxide of the atmosphere. The crucible should be kept *tightly covered* in the desiccator during cooling to prevent the taking-up of water from the atmosphere of the desiccator. It must be remembered that after opening the desiccator the humidity of the air therein may not be very different from that of the external atmosphere. Pure concentrated sulfuric acid, freshly ignited calcium oxide, or an equally vigorous desiccant should be used as drying agent; calcium chloride is not suitable. In any case, the crucible and its contents should not be allowed to remain in the desiccator longer than is necessary. The crucible should likewise be kept covered during the weighing; and this operation should be performed rapidly, the final weighing being made with all the weights on the pan, and the rider adjusted.

Although satisfactory results can be obtained by weighing calcium as the oxide, it is preferable to weigh as the carbonate if the proper facilities are available, because the latter weighing form is not appreciably hygroscopic and has a much higher molecular weight.

Calcium sulfate. By treating calcium oxalate, carbonate, or oxide with an excess of sulfuric acid, evaporating the latter, and igniting the residue to the proper temperature, anhydrous calcium sulfate is obtained. Calcium sulfate is not easily decomposed by heating; the temperature of beginning decomposition,

$$CaSO_4 \rightarrow CaO + SO_3,$$

is given as 1200°, but the decomposition may set in at a lower temperature if foreign substances are present. Calcium sulfate may safely be heated over a Tirrill flame to moderate redness. If the residue is not heated strongly enough, traces of water remain, and the results are slightly high.

Calcium sulfate would be a good weighing form for calcium were it not for the fact that the conversion of the precipitate into the sulfate is attended with some difficulties. The precipitate must of course be collected on paper, and the latter must be burned before the conversion is attempted. If the precipitate is not separated from the filter paper, carbonate is formed during the ignition; there will consequently be an evolution of carbon dioxide when sulfuric acid is subsequently added, and this is likely to lead to loss even if the crucible is covered. In this case, therefore, it is better to ignite strongly to convert most of the carbonate to the oxide and to add water rapidly to the cold residue to slake the oxide. Sulfuric acid is then added. Or the dried precipitate is separated from the filter paper and reserved, while the paper, with a small amount of adhering precipitate, is ignited to burn away all the carbon. The main portion of the precipitate is then added, and the whole is treated with dilute sulfuric acid. In any case, a rather large excess of dilute sulfuric acid is added to insure the conversion of the residue into sulfate, the conversion being hindered by the tendency of the slightly soluble calcium sulfate to form as a coating over the particles of the residue.[1] The excess sulfuric acid is removed by volatilization in a radiator (p. 184), and the final ignition is made over a medium Tirrill flame. A porcelain crucible may be used in this procedure.

Calcium fluoride. By treating calcium oxalate, carbonate, or oxide with excess hydrofluoric acid as described above for calcium sulfate, evaporating and igniting the residue, anhydrous calcium fluoride is obtained. Calcium fluoride may be heated to redness without fear of decomposition, and it is not hygroscopic. A platinum crucible is required for this conversion. This weighing form is rarely used.

✓

Separation of calcium from magnesium by the oxalate method.

It will be seen from Table LII that the solubility of magnesium oxalate in aqueous solutions is relatively small, and hence it is to be expected that a sharp separation of calcium from magnesium by precipitation with oxalate is not easily accomplished. There is in the first place the danger that magnesium oxalate will actually be precipitated owing to its limited solubility, unless proper care is taken. There is also the possibility that magnesium oxalate will be appreciably occluded by calcium oxalate in accordance with the coprecipitation rule (p. 120), which states that the tendency of a compound having an ion in common with the lattice of the precipitate to be adsorbed by the growing precipitate increases with decreasing solubility of the compound. Lastly, the solubility of calcium oxalate in the presence of a high concentration of magnesium ion is a source of error which must be taken into consideration when the ratio of magnesium to calcium is large.

---

[1] Dissolving the slaked lime in a little hydrochloric acid before the addition of sulfuric acid is therefore to be recommended.

TABLE LII. SOLUBILITY OF MAGNESIUM OXALATE IN WATER AND AMMONIUM OXALATE SOLUTIONS AT ROOM TEMPERATURE

CONCENTRATION OF $(NH_4)_2C_2O_4 \cdot H_2O$ G. PER 100 ML. OF SOLUTION	SOLUBILITY OF $MgC_2O_4 \cdot 2\ H_2O$ AT 22 ± 1° G. PER 100 ML. OF SOLUTION
0	0.036
1	0.059
2	0.095
3	0.133
4	0.187

The danger of separation of magnesium oxalate as such is diminished by the tendency of this salt to form supersaturated solutions which are quite stable under certain conditions.[1]

The greater the degree of supersaturation, the greater is the danger of precipitation of magnesium oxalate. The supersaturation is quickly broken down when the solutions are boiled; and, in general, equilibrium is more rapidly established the higher the temperature. Solutions of magnesium oxalate having a high degree of supersaturation sooner or later deposit magnesium oxalate on standing at room temperature, although it may take some time for crystallization to begin and, once started, it will usually be quite slow unless the temperature is raised. Therefore when calcium oxalate is to be precipitated in the presence of magnesium, the temperature of the solution should not be too high, and boiling must especially be avoided. It has been shown experimentally that by using a considerable excess of ammonium oxalate in the precipitation as directed in the procedure following, as much as 150 mg. of magnesium may be present in 200 to 250 ml. of solution without danger of precipitation of magnesium oxalate. If much more magnesium than this is present, there is the possibility that there will be a slow deposition of magnesium oxalate on standing, especially if the solution is kept warm. The postprecipitation of magnesium oxalate is to be avoided, because when it occurs there is great danger that a double, or sometimes even a triple, precipitation of calcium oxalate will not yield a precipitate free from magnesium.

---

[1] W. Fischer, Z. anorg. allgem. Chem. *153*, 62 (1926).

Even when the conditions are such that magnesium cannot precipitate as the oxalate, it is found that the calcium precipitate is contaminated to a greater or lesser extent by occluded magnesium oxalate. The amount of magnesium which is coprecipitated depends upon the conditions of precipitation, as the results in Table LIII indicate. It is especially interesting to note that the calcium precipitate obtained by neutralizing a strongly acid calcium-magnesium solution containing a relatively large amount of ammonium oxalate with ammonium hydroxide contains very little magnesium. The decrease in the magnesium coprecipitation under these conditions is to be ascribed to the excess of ammonium oxalate present during the whole course of the precipitation. The solubility of magnesium oxalate is thereby increased, and complex magnesio-oxalate ions are formed. It follows, then, that the precipitation of calcium in the presence of magnesium should be made by neutralizing an acid solution containing a considerable excess of ammonium oxalate and not by adding oxalate to an ammoniacal solution of calcium-magnesium, as has frequently been recommended. There is only one objection to the addition of *very* large amounts of ammonium oxalate, and that is the interference of ammonium salts, especially of the oxalate, in the determination of magnesium (p. 371). It is true that the ammonium oxalate may be destroyed prior to the determination of magnesium, but this may not always be convenient. In any case, however, it is necessary to add a fairly large excess of ammonium oxalate to precipitate calcium oxalate quantitatively, because, as already mentioned, magnesium ions withdraw oxalate ions forming a complex oxalate, thus increasing the solubility of calcium oxalate. Calcium does not form a complex with oxalate, and the solubility of calcium oxalate therefore decreases with increasing oxalate concentration and remains negligibly small even in warm 20 per cent ammonium oxalate.

In most cases a double precipitation of calcium oxalate must be made to secure a precipitate free from magnesium, even when the precipitation is made under favorable conditions. Thus in Experiment 7, Table LIII, a single precipitation of calcium from an acid solution containing 2.5 per cent of ammonium oxalate gave a precipitate containing nearly 0.2 mg. of magnesium to 100 mg. of calcium, equal amounts of the two metals being originally present. This amount of coprecipitated magnesium would be of no consequence in routine analysis but has to be taken into account in more accurate work.

It may be mentioned that, as ordinarily carried out, the oxalate method for the separation of calcium from magnesium fails when the ratio of magnesium to calcium is very large. However, by using a very large excess of ammonium oxalate to keep magnesium in solution, it is possible to separate as little as one part of calcium from one hundred parts of magnesium.[1] If a large excess of ammonium oxalate is not added, calcium is precipitated incompletely or not at all. Such unprecipitated calcium is subsequently quantitatively precipitated as the phosphate with magnesium ammonium phosphate in the determination of magnesium and can be recovered by the method of Hillebrand.[1] In this procedure the ignited residue of magnesium pyrophosphate (p. 372) is dissolved in a small excess of dilute sulfuric acid, and the solution is treated with a large excess of 75 per cent ethyl alcohol. Calcium sulfate is insoluble in the alcoholic solution, whereas magnesium sulfate is quite soluble and is not precipitated. The precipitate of calcium sulfate is filtered off, washed with 75 per cent alcohol, dissolved in hydrochloric acid, and the calcium then precipitated as the oxalate and weighed as the oxide. The true weight of magnesium pyrophosphate is found by deducting the weight of $Ca_3(PO_4)_2$ corresponding to the weight of calcium found from the weight of the impure magnesium pyrophosphate.

---

[1] M. Bobtelsky and Frau Malkowa-Janowski, Z. angew. Chem. *40*, 1436 (1927).

Procedure. The following directions provide for the presence of magnesium and the alkali metals but no other cations.

Prepare in water or hydrochloric acid a solution of the sample containing not more than 200 mg. of calcium or 100 to 150 mg. of magnesium, dilute to 200 ml., and add a few drops of methyl red indicator. Add 5 ml. of concentrated hydrochloric acid in excess and then 50 ml. of a warm ammonium oxalate solution[2] containing 3 g.[3] of $(NH_4)_2C_2O_4 \cdot H_2O$. Heat the solution to 70°–80°, and add 1 : 1 ammonium hydroxide dropwise with stirring until the color changes from red to yellow. Allow the solution to stand without further heating for one hour (not longer if magnesium is present),[4] and filter through paper. Wash the precipitate four or five times with cold 0.1 per cent ammonium oxalate solution, and then dissolve it in 50 ml. of hot 1 : 4 hydrochloric acid. Wash the paper with hot 1 : 100 hydrochloric acid, and dilute the solution to 200 ml. Add 1 g. of ammonium oxalate dissolved in a few ml. of hot water, heat the solution nearly to boiling, and precipitate calcium oxalate again by neutralizing the acid solution with ammonium hydroxide as already described. Allow the solution to stand for an hour or two (longer standing will now do no

---

[1] W. F. Hillebrand, *Analysis of Silicate and Carbonate Rocks*, Bull. No. 700, U. S. Geol. Survey, p. 152.

[2] This solution should be filtered hot if not entirely clear.

[3] If magnesium is not to be determined, add 5 to 6 g. of ammonium oxalate. A like amount may be added if the oxalate is later destroyed by nitric acid (p. 382) prior to the determination of magnesium. If calcium alone is present, add only 1 g. of ammonium oxalate in excess, and do not reprecipitate unless sodium is present. In the absence of magnesium make the precipitation at 100°.

[4] It is advisable to stir occasionally to disperse the precipitate through the solution and so aid the precipitation of the last traces of calcium which tend to remain in supersaturated solution, especially if the amount of precipitate is small.

TABLE LIII. COPRECIPITATION OF MAGNESIUM OXALATE WITH CALCIUM OXALATE UNDER VARIOUS CONDITIONS [1]

In each experiment 100 mg. of calcium and 100 mg. of magnesium as chlorides were present in 200 ml. of solution. The solution was allowed to stand one to two hours after precipitation, the precipitate filtered off, washed, dissolved in hydrochloric acid, and reprecipitated by addition of ammonium hydroxide; the magnesium in the filtrate from the reprecipitated calcium oxalate was precipitated with 8-hydroxyquinoline and the precipitate titrated.

CONDITION OF PRECIPITATION	MAGNESIUM (Mg) IN CALCIUM OXALATE PRECIPITATE (100 mg. Ca)
	mg.
1. 11 ml. of 0.5 *N* (3.5 per cent) ammonium oxalate solution added dropwise over a period of 3 minutes to the cold (20°–25°) neutral calcium-magnesium solution. An excess of 5 g. of ammonium oxalate in 50 ml. of water then added	0.33
2. Conditions as in (1) except that the 0.5 *N* ammonium oxalate solution was added dropwise to the calcium-magnesium solution *heated to 70°*	0.70
3. Precipitated as in (2) in hot (70°) solution, but calcium-magnesium solution was made ammoniacal before precipitation by adding 2 ml. of concentrated ammonium hydroxide and 1 g. of ammonium chloride	0.64
4. Precipitated as in (2) in hot (70°) solution, but calcium-magnesium solution was made acid before precipitation by adding 5 ml. of 6 *N* acetic acid	1.06
5. 50 ml. of hot 10 per cent ammonium oxalate solution added very rapidly (5 seconds) to neutral calcium-magnesium solution heated to 70°	1.26
6. Calcium-magnesium solution acidified with 5 ml. of concentrated hydrochloric acid, heated to 70°, and treated with 11 ml. of 0.5 *N* ammonium oxalate. No precipitate formed. Then made ammoniacal by adding dilute ammonium hydroxide over a period of 2 minutes	0.66
7. 50 ml. of hot 10 per cent ammonium oxalate solution added rapidly to hot (70°) calcium-magnesium solution containing 5 ml. of concentrated hydrochloric acid. After 5 minutes the solution was neutralized with dilute ammonium hydroxide	0.16
8. Conditions as in (7) except that precipitation was made at room temperature	0.15
9. 100 mg. of calcium and 100 mg. of magnesium as chlorides dissolved in 50 ml. of water, and the solution added slowly (5 minutes) to 200 ml. of warm (70°) ammonium oxalate solution containing 5 g. of the salt	0.72

---

[1] Unpublished results of E. B. Sandell.

harm). Collect the precipitate in a weighed porcelain filter or Gooch crucible if calcium carbonate is to be used as the weighing form, or in filter paper if the precipitate is to be ignited to the oxide. Wash the precipitate thoroughly with cold 0.1 per cent ammonium oxalate solution. Reserve the filtrates and washings from the first and second precipitations if magnesium is to be determined (p. 382).

If the precipitate is to be ignited to the carbonate, dry the crucible first at a low temperature, and then place it in an electric furnace regulated to the temperature 500°. The temperature should not vary by more than ± 25° from this value. After one or two hours remove the crucible, cool, and weigh. Repeat the heating to constant weight, using 30-minute periods of heating. Finally, to be sure that no decomposition of calcium carbonate has occurred, moisten the residue with 2 or 3 drops of saturated ammonium carbonate solution, allow to stand at room temperature for 15 minutes, dry at 110° to 120° for one-half hour, and weigh. There should be no change in weight. If an increase in weight is found, repeat the moistening with ammonium carbonate and heating until the weight is constant.

When the oxide is to be used as the weighing form, place the paper with the precipitate in a platinum crucible, char the filter at a low temperature, and then heat strongly for 15 to 30 minutes over a Meker burner or blast lamp. Keep the crucible covered except after the start of the strong heating, when the cover should be displaced to one side for a short time to allow the escape of carbon dioxide. Do not allow the flame gases to gain access to the interior of the crucible. Cool the covered crucible in a desiccator filled with sulfuric acid or similar effective drying agent. Do not permit the crucible to stand unnecessarily long in the desiccator. Weigh as rapidly as possible, and of course keep the crucible covered. Reheat strongly for 10 or 15 minutes and weigh again, first placing the weights on the pan so that only the rider or chain need be adjusted after the crucible is placed on the balance. Repeat the ignition until constant weight is obtained.

If a porcelain crucible is used for igniting the precipitate to the oxide, employ an electric muffle furnace, and heat to 1000° to 1100°.

Calculate the percentage of calcium or calcium oxide.

Regarding the recovery of any calcium that may have escaped precipitation, see page 358.

PROBLEMS

1. 250 ml. of tap water gave an ignited calcium oxide residue weighing 0.0476 g. Calculate the calcium content of the water in p.p.m. (mg. per liter) of calcium carbonate. *Ans.* 338.

2. What volume of 0.050 *M* calcium chloride solution must be taken to furnish 1.00 g. of calcium carbonate? *Ans.* 200 ml.

3. Calculate the solubility of $CaC_2O_4 \cdot H_2O$ in a solution of pH 5.0 which is 0.05 *M* in oxalate.

4. If the solubility of $CaC_2O_4 \cdot H_2O$ in water at 95° is 14.0 mg. per liter, what will be the solubility in a 0.05 *M* potassium oxalate solution at the same temperature?

5. An ignited residue of calcium carbonate contains 1.0 per cent of CaC_2O_4. What error (in p.p. thousand of Ca) is made if it is assumed that the weighed residue consists entirely of calcium carbonate? *Ans.* + 2.2 p.p.t.

6. What volume of sulfuric acid of sp. gr. 1.24 containing 32.3 per cent H_2SO_4 is theoretically required to convert 0.75 g. of $CaC_2O_4 \cdot H_2O$ into $CaSO_4$? *Ans.* 1.26 ml.

CHAPTER XXII

DETERMINATION OF MAGNESIUM

Two gravimetric methods for the determination of magnesium are considered in this chapter. The first method to be described is an old one that has been employed since the first part of the nineteenth century and is still commonly used. The second method is a recent one (1927) and furnishes a good example of the use of an organic precipitant in quantitative analysis.

I. Determination of magnesium by precipitation as magnesium ammonium phosphate and ignition of the precipitate to magnesium pyrophosphate.

Method. An acid solution of the sample is treated with an excess of ammonium phosphate, and an excess of strong ammonium hydroxide is then added at room temperature to precipitate magnesium ammonium phosphate:

$$Mg^{++} + NH_4^+ + PO_4^{\equiv} + 6\ H_2O \rightarrow MgNH_4PO_4 \cdot 6\ H_2O.$$

The precipitate thus obtained does not have quite the theoretical composition for reasons to be mentioned later, and it is therefore dissolved in dilute hydrochloric acid after washing with a dilute solution of ammonia and is reprecipitated by the addition of excess ammonium hydroxide. A small amount of ammonium phosphate is added in the second precipitation to reduce the solubility of the precipitate. The pure precipitate thus obtained is washed with dilute ammonium hydroxide, ignited to magnesium pyrophosphate at a high temperature (1100°), and weighed as such:

$$2\ MgNH_4PO_4 \rightarrow Mg_2P_2O_7 + 2\ NH_3 + H_2O.$$

Solubility of magnesium ammonium phosphate. Magnesium ammonium phosphate is one of the most soluble precipitation forms used in quantitative analysis. The equilibrium involved in solutions of magnesium ammonium phosphate is very complicated. Naturally, according to the mass-action law we will find that in any solution saturated with the magnesium ammonium phosphate the following relation holds:

$$[Mg^{++}][NH_4^+][PO_4^{\equiv}] = S_{MgNH_4PO_4 \cdot 6\ H_2O}$$

in which S denotes the solubility product.

In a saturated solution of the salt in water, part of the NH_4^+ ions will be transformed into NH_4OH. This equilibrium is governed by the hydroxyl-, and hence by the hydrogen-ion concentration:

$$NH_4^+ + OH^- \rightleftarrows NH_4OH$$

and
$$\frac{[NH_4^+]}{[NH_4OH]} = \frac{K_{NH_3}}{[OH^-]} = \frac{K_{NH_3}}{K_w} \cdot [H^+]$$

in which K_{NH_3} is the ionization constant of ammonium hydroxide and K_w the ionization product of water (see p. 37 and p. 38). The trivalent phosphate ions are strongly hydrolyzed, the amount transformed into $HPO_4^=$ and $H_2PO_4^-$ being dependent upon the hydrogen-ion concentration of the solution and the third and second ionization constants of phosphoric acid:

$$PO_4^{\equiv} + H^+ \rightleftarrows HPO_4^= \text{ (third ionization)}$$
$$HPO_4^= + H^+ \rightleftarrows H_2PO_4^- \text{ (second ionization).}$$

A saturated solution of magnesium ammonium phosphate in water therefore will contain the following components: Mg^{++}; NH_4^+, NH_4OH; $PO_4^{\equiv}$, $HPO_4^=$, $H_2PO_4^-$.

If the molar solubility of the salt is equal to c, then

$$[Mg^{++}] = c$$
$$[NH_4^+] + [NH_4OH] = c$$
$$[PO_4^{\equiv}] + [HPO_4^=] + [H_2PO_4^-] = c.$$

With known c, known hydrogen-ion concentration, and the known values of the various ionization constants, it is possible to calculate $[NH_4^+]$ and $[PO_4^{\equiv}]$ in the saturated solution and therefore also the solubility product. Unfortunately no exact data are available. However, it is doubtful whether the figures would have an exact significance, since the solid phase probably is not stable in contact with water. From the above it is evident that the solubility of the magnesium ammonium phosphate will be smaller in a mixture of ammonia and ammonium chloride than in water. In the first place the excess of ammonium ions repress the solubility according to the mass-action law:

$$[Mg^{++}][NH_4^+][PO_4^{\equiv}] = S,$$

and besides, the excess of ammonia lowers the hydrogen-ion concentration, thereby decreasing the hydrolysis of the $PO_4^{\equiv}$ ions.

In the quantitative determination of magnesium an excess of ammonium phosphate is present in the solution containing ammonia and ammonium ions. Since the ammonium ions repress the dissociation of ammonium hydroxide, $[NH_3]$ and $[NH_4^+]$ may be taken equal to the analytical concentrations of ammonia and ammonium salts respectively. On the other hand, the hydrolysis of the phosphate ions is appreciable.

$$PO_4^{\equiv} + H_2O \rightleftarrows HPO_4^= + OH^-$$
$$HPO_4^= + H_2O \rightleftarrows H_2PO_4^- + OH^-.$$

As a result of this hydrolysis, $[PO_4^{\equiv}]$ is much smaller than the analytical concentration of ammonium phosphate present.

Let us assume that the concentration of free ammonia in the supernatant liquid is 1 M and that of ammonium ion is 0.18 M. From the ionization constant of ammonia it is found that:

$$[\mathrm{OH^-}] = \frac{[\mathrm{NH_4OH}]}{[\mathrm{NH_4^+}]} K_{\mathrm{NH_3}} = \frac{1}{0.18} \times 1.8 \times 10^{-5} = 10^{-4}$$

and $$[\mathrm{H^+}] = \frac{K_w}{[\mathrm{OH^-}]} = \frac{10^{-14}}{10^{-4}} = 10^{-10}\ (25°).$$

Let us further assume that the excess of ammonium phosphate in the supernatant liquid corresponds to a concentration of 0.02 *M*.

$$[\mathrm{PO_4^{\equiv}}] + [\mathrm{HPO_4^=}] + [\mathrm{H_2PO_4^-}] = 0.02.$$

The third ionization constant of phosphoric acid is of the order of 5×10^{-13};

therefore $$\frac{[\mathrm{H^+}][\mathrm{PO_4^{\equiv}}]}{[\mathrm{HPO_4^=}]} = 5 \times 10^{-13}$$

and since $[\mathrm{H^+}]$ has been taken equal to 10^{-10} it is found that

$$\frac{[\mathrm{PO_4^{\equiv}}]}{[\mathrm{HPO_4^=}]} = 5 \times 10^{-3} = 0.005. \qquad (1)$$

The second ionization constant of phosphoric acid is 7.5×10^{-8}.

Therefore $$\frac{[\mathrm{HPO_4^=}]}{[\mathrm{H_2PO_4^-}]} = \frac{7.5 \times 10^{-8}}{10^{-10}} = 750. \qquad (2)$$

From (1) and (2) it follows that virtually all of the phosphate is present in the form of $\mathrm{HPO_4^=}$. Since the total phosphate concentration was taken equal to 0.02 *M*, it is found from equation (1) that

$$[\mathrm{PO_4^{\equiv}}] = 5 \times 10^{-3} \times 0.02 = 10^{-4}.$$

The amount of magnesium unprecipitated is determined by the solubility product of magnesium ammonium phosphate, and the ammonium and phosphate ion concentrations: $$[\mathrm{Mg^{++}}] = \frac{S_{\mathrm{MgNH_4PO_4}}}{[\mathrm{NH_4^+}][\mathrm{PO_4^{\equiv}}]}. \qquad (3)$$

It is readily seen now that with the same excess of ammonium and total phosphate in the solution, the amount of magnesium left in solution within a certain pH range increases linearly with the hydrogen-ion concentration.

If by varying the concentration of free ammonia the hydrogen-ion concentration were made equal to 10^{-9}, all other concentrations being kept the same as in the above case, it would be found that $[\mathrm{PO_4^{\equiv}}]$ would be equal to 0.0005 instead of 0.005 *M*, and the amount of magnesium left in the solution would be ten times greater than in the previous case (equation 3).

From the above it is evident that the solubility of magnesium ammonium phosphate in dilute ammonia is much less than in water. Use is made of this fact in washing the precipitate.

In the precipitation of phosphate as magnesium ammonium phosphate (see Chapter XXIV), the supernatant liquid contains an excess of magnesium, ammonium ions, and ammonia. The amount of trivalent phosphate ion left in solution is given by the expression:

$$[\mathrm{PO_4^{\equiv}}] = \frac{S_{\mathrm{MgNH_4PO_4}}}{[\mathrm{NH_4^+}][\mathrm{Mg^{++}}]}.$$

From this, one might infer that the addition of a large excess of ammonium ions would be desirable in order to decrease the solubility as much as possible. This, however, is not true, since the trivalent phosphate ions are hydrolyzed:

$$PO_4^{\equiv} + H_2O \rightleftarrows HPO_4^{=} + OH^-.$$

This hydrolysis — and therefore also the solubility and the amount of phosphate not precipitated — increases with increasing ammonium-ion concentration. Given the excess of ammonia and of magnesium ions, the ammonium-ion concentration at which the solubility of the precipitate is a minimum can be calculated.

To avoid losses due to solubility, the precipitation of magnesium ammonium phosphate is made in relatively small volumes of solution, and care is taken to have the solution cold at the time of filtration. Since the precipitate tends to form supersaturated solutions, the precipitation mixture is allowed to stand for some time, preferably overnight, before filtration. For the reason already stated, the precipitate is washed with cold dilute ammonium hydroxide. A 1 : 20 solution of ammonium hydroxide is a suitable wash liquid. Under the conditions recommended in the procedure below, less than 0.1 mg. of magnesium should be lost in double precipitations as a result of solubility.[1]

Precipitation of magnesium ammonium phosphate. *Possible contaminants of the precipitate.* In order that the ignited magnesium ammonium phosphate precipitate may consist entirely of magnesium pyrophosphate, it is necessary that the precipitate be composed entirely of $MgNH_4PO_4$. As will be shown later, a precipitate contaminated with other phosphates will not give pure magnesium pyrophosphate on ignition, and erroneous results will then necessarily be obtained. It is by no means an easy matter to obtain a pure precipitate of magnesium ammonium phosphate, as the extensive literature on the subject indicates.[2] The difficulty arises from the coprecipitation of ammonium phosphates and magnesium phosphates.

---

[1] J. I. Hoffman and G. E. F. Lundell, Bur. Standards J. Research *5*, 288 (1930).

[2] Following are some references to the precipitation of magnesium ammonium phosphate:

W. Gibbs, Am. J. Sci. [3], *5*, 114 (1873).

H. Neubauer, Z. anal. Chem. *43*, 14 (1904); Z. angew. Chem. *9*, 435 (1896).

F. A. Gooch and M. Austin, Am. J. Sci. [4], *7*, 187 (1899); Z. anorg. Chem. *20*, 121 (1899); Chem. News *79*, 233, 244, 255 (1899).

K. K. Järvinen, Z. anal. Chem. *44*, 335 (1905).

B. Schmitz, Z. anal. Chem. *45*, 512 (1906); *65*, 46 (1924).

K. Bube, Z. anal. Chem. *49*, 587 (1910).

Z. Karaoglanow and P. Dimitrow, Z. anal. Chem. *57*, 353 (1918).

D. Balarew, Z. anorg. Chem. *101*, 225 (1917).

G. Jörgensen, Analyst *51*, 61 (1926).

A. Epperson, J. Am. Chem. Soc. *50*, 321 (1928).

J. I. Hoffman and G. E. F. Lundell, Bur. Standards J. Research *5*, 279 (1930).

Magnesium forms the slightly soluble phosphates, $MgHPO_4 \cdot aq.$, and $Mg_3(PO_4)_2 \cdot aq.$ When an excess of ammonium hydroxide is added to an acid solution of a magnesium salt containing ammonium phosphate (the recommended method of making the precipitation), the possible precipitation of the preceding phosphates must be considered. As long as there is a sufficient concentration of ammonium salt in the solution, the precipitation of magnesium hydroxide is excluded. The substance or substances precipitated will depend upon the solubility products of the various possible compounds, and the concentrations of $PO_4^{\equiv}$, $HPO_4^{=}$, $H_2PO_4^-$, and NH_4^+ in a particular solution. In a solution of a phosphate the following equilibria exist:

$$\begin{array}{ccccccc} H_3PO_4 & \rightleftarrows & H_2PO_4^- & \rightleftarrows & HPO_4^{=} & \rightleftarrows & PO_4^{\equiv}. \\ & & +H^+ & & +H^+ & & +H^+ \\ \longleftarrow & & & & & \longrightarrow & \\ \textit{(acid solutions)} & & & & \textit{(alkaline solutions)} & & \end{array}$$

In the determination of magnesium there is no danger of the precipitation of $Mg(H_2PO_4)_2$ because the solubility of the acid phosphate is relatively great. As the addition of ammonium hydroxide to the acid magnesium solution is continued, the danger of precipitation of $MgHPO_4$ and $Mg_3(PO_4)_2$ increases, because the concentrations of $HPO_4^{=}$ and $PO_4^{\equiv}$ are increased. If in the meantime the solubility product of $MgNH_4PO_4$ has been exceeded, this phosphate will be precipitated; and there is then less danger of the precipitation of the other phosphates. It is rather easy to arrange conditions during the precipitation so that only $MgNH_4PO_4$ will be precipitated upon the addition of ammonia to the acid solution. It is difficult, however, to prevent the *coprecipitation* of other phosphates during the precipitation.

TABLE LIV. IGNITION PRODUCTS OF POSSIBLE CONTAMINANTS OF MAGNESIUM AMMONIUM PHOSPHATE

CONTAMINANT	IGNITION PRODUCT	PROBABLE DIRECTION OF ERROR IN DETERMINATION OF MAGNESIUM
H_3PO_4	$HPO_3 + P_2O_5$ [a]	Positive
$NH_4H_2PO_4$	$HPO_3 + P_2O_5$	Positive
$(NH_4)_2HPO_4$	$HPO_3 + P_2O_5$	Positive
$(NH_4)_3PO_4$	$HPO_3 + P_2O_5$	Positive
$Mg(H_2PO_4)_2$	$Mg(PO_3)_2$; $Mg_2P_2O_7$	Positive
$MgHPO_4$	$Mg_2P_2O_7$	None
$Mg_3(PO_4)_2$	$Mg_3(PO_4)_2$	Negative
Basic magnesium phosphates	$Mg_3(PO_4)_2 + MgO$	Negative
$Mg(OH)_2$	MgO	Negative
$MgCl_2$	Chiefly MgO	Negative
NH_4Cl	(Volatile)	None

[a] Volatilizes on long-continued ignition at elevated temperatures (1000° to 1100°).

The possibility of contamination of magnesium ammonium phosphate through coprecipitation is especially great because of the numerous substances that may be carried down: H_3PO_4, $(NH_4)H_2PO_4$, $(NH_4)_2HPO_4$, $(NH_4)_3PO_4$, $Mg(H_2PO_4)_2$, $MgHPO_4$, $Mg_3(PO_4)_2$, basic magnesium phosphates, $Mg(OH)_2$, $MgCl_2$, and NH_4Cl. Of these it is necessary to consider only the ammonium and magnesium phosphates, which have a special tendency to coprecipitate owing to the presence of ammonium, magnesium, and phosphate ions in the lattice of the precipitate. The effect of the presence of these contaminants on the determination of magnesium by the pyrophosphate method is indicated in Table LIV, which gives the ignition product of the various contaminants. It is to be noted that coprecipitation of the ammonium phosphates and $Mg(H_2PO_4)_2$ leads to high results for magnesium, and the coprecipitation of $Mg_3(PO_4)_2$, basic phosphates, and $Mg(OH)_2$ to low results; the presence of $MgHPO_4$ causes no error, for this compound gives the pyrophosphate on ignition.

Effect of conditions of precipitation upon nature of coprecipitated substances. It is interesting to consider the effect of the conditions of precipitation of magnesium ammonium phosphate upon the kind of coprecipitation. For the sake of illustration three cases will be considered, which have their counterparts in methods of precipitation that have been recommended in the literature:

1. The phosphate solution is added to a strongly ammoniacal solution of magnesium containing a relatively low concentration of ammonium salts. After ignition of the precipitate it is found that the residue weighs less than it should. This result is usually explained as being due to the *precipitation* of $Mg_3(PO_4)_2$. Actually there is a coprecipitation of this compound, or perhaps of a basic magnesium phosphate. It is evident that the conditions of precipitation are favorable for the adsorption and occlusion of these substances owing to the high pH of the solution. The probability of coprecipitation of ammonium phosphate, $(NH_4)_3PO_4$, is small because it is not in excess during the precipitation.

2. The phosphate solution is added to a neutral or slightly ammoniacal solution of magnesium salt containing considerable amounts of ammonium salts. The results for magnesium are generally found to be high after the precipitate has been ignited, as a result of the coprecipitation of ammonium phosphates such as $(NH_4)_2HPO_4$ and $NH_4H_2PO_4$. Upon ignition these yield metaphosphoric acid and phosphorus pentoxide, which are only difficultly volatile at the temperature of ignition.

3. An acid solution of a magnesium salt containing excess ammonium phosphate is slowly neutralized with ammonium hydroxide. After ignition the precipitate weighs more than it should. Under the conditions given there is a possibility of the coprecipitation of $Mg(H_2PO_4)_2$, $MgHPO_4$, and ammonium phosphates. The presence of $Mg(H_2PO_4)_2$ is likely to lead to high values for magnesium, because it decomposes into $Mg(PO_3)_2$ on ignition and this phosphate loses P_2O_5 only slowly at high temperatures, finally, however, giving $Mg_2P_2O_7$. The presence of $MgHPO_4$ leads to no error, but again ammonium phosphates in the precipitate cause high results. The higher the concentration of ammonium salts, especially ammonium phosphate in solution, the greater will be the tendency for ammonium phosphate to be coprecipitated,

and the higher the results will be as long as the solubility of the precipitate is not unduly increased.[1]

Rationale of the double precipitation of magnesium ammonium phosphate. It is virtually impossible to determine magnesium accurately by a single precipitation of magnesium ammonium phosphate, unless the amount of magnesium present is known beforehand so that too large an excess of ammonium phosphate can be avoided, and large amounts of ammonium salts are not present. Usually these conditions cannot be met, especially in systematic analyses where separations, resulting in accumulation of ammonium salts in the solution, have preceded the precipitation of magnesium. However, if the element can be precipitated quantitatively the first time, it is relatively easy to obtain an accurate determination of the magnesium by dissolving the precipitate in dilute hydrochloric acid and reprecipitating with ammonium hydroxide under the proper conditions. It is easy to understand why a second precipitation will give a precipitate of the proper composition. In the reprecipitation the amount of ammonium salt can be controlled, and the excess of ammonium phosphate can

TABLE LV. EFFECT OF CONDITIONS ON THE DETERMINATION OF MAGNESIUM BY THE PYROPHOSPHATE METHOD[2]

The determinations were made substantially as described in the procedure on p. 371, except as indicated in the first column.

VARIATION IN STANDARD PROCEDURE	NUMBER OF PRECIPITATIONS	$Mg_2P_2O_7$ (AS $MgCl_2$) TAKEN	$Mg_2P_2O_7$ FOUND
Excess NH_4Cl g.		g.	g.
1	1	0.1156	0.1179
5	1	0.1156	0.1180
10	1	0.1156	0.1189
16	2	0.1367	0.1367
0	2	0.1156	0.1161
Excess NH_4OH ml.			
25	1	0.1367	0.1395
25	2	0.1367	0.1367
Excess $(NH_4)_2HPO_4$ 150 ml. saturated solution	2	0.1367	0.1370

---

[1] Confirmed by the experimental results of A. W. Epperson, J. Am. Chem. Soc. *50*, 321 (1928). Cf. Table LV.

[2] Figures taken from tables given by A. W. Epperson, J. Am. Chem. Soc. *50*, 321 (1928).

be limited to the small amount required to reduce the solubility of the precipitate. The conditions are such that no appreciable amount of ammonium phosphate is coprecipitated, and the main source of error is thereby eliminated.

In the reprecipitation, the precipitate is dissolved in dilute hydrochloric acid, too large an excess being avoided, a very small amount of ammonium phosphate is added, and an excess of ammonium hydroxide is then slowly added at room temperature. Care must be taken to limit the ammonium-ion, and especially the phosphate-ion, concentration to relatively low values, or the second precipitate will also be contaminated with ammonium phosphate. The procedure for the determination of magnesium, as here briefly described and given in detail on p. 371, has been shown to give accurate results.[1]

Ignition of the precipitate. The precipitate of magnesium ammonium phosphate is usually ignited to magnesium pyrophosphate at a high temperature and weighed as such. It has been proposed to weigh the precipitate in the form of the hexahydrate after washing with alcohol and ether and allowing the latter to evaporate at room temperature.[2] In the latter method it is always necessary to precipitate at room temperature to insure the presence of magnesium ammonium phosphate entirely in the form of the hexahydrate. At higher temperatures there is danger that the monohydrate will be formed. It is stated that the transition temperature for the transformation of the hexahydrate into the monohydrate lies at 40° to 60°.[3] This method of weighing the precipitate has not been generally adopted for accurate work. There is always great danger in weighing a substance after drying at room temperature, owing to the possible presence of nonessential water. It is safer to ignite the precipitate to the pyrophosphate.

The ignition of magnesium ammonium phosphate to magnesium pyrophosphate is best made at 1100° in an electric furnace; at this temperature the residue can be heated for prolonged periods without decomposition. At 1200° the pyrophosphate slowly loses in weight, and at 1000° the precipitate only slowly comes to constant weight.[1] The ignition may be made in porcelain or platinum crucibles.

---

[1] A. W. Epperson, J. Am. Chem. Soc. *50*, 321 (1928); J. I. Hoffman and G. E. F. Lundell, Bur. Standards J. Research *5*, 279 (1930)

[2] For an example of such a procedure see L. W. Winkler, Z. angew. Chem. *31*, 211 (1918).

[3] The exact temperature depends upon the composition of the solution. See K. Bube, Z. anal. Chem. *49*, 587 (1910).

Burning off the carbon of the filter paper requires greater care in the case of magnesium ammonium phosphate than in the case of most precipitates. In the first place, there is danger of reduction of the phosphate precipitate if the heating is strong while carbon still remains, with the possibility of injury to the platinum crucible, if such is used, by the reduced phosphorus; at high temperatures there is some loss of phosphorus when carbon is heated with pyrophosphate.[2] Moreover, if the heating is rapid at first, the residue is blackened by the carbon resulting from the decomposition of the carbonaceous products of the paper, and this carbon is so intimately associated with the particles of the residue that it remains even after prolonged heating at high temperatures; sometimes an apparently white residue will contain a core of very dark material.[3] The formation of a dark residue can be prevented by charring the paper and burning off the carbon at as low a temperature as possible. The temperature must be raised very gradually in the process. If a burner is used, the reducing gases of the flame must not be allowed to gain access to the contents of the crucible. The ignited residue is usually somewhat gray, not pure white.

A porcelain filter crucible may be used to collect the precipitate. The crucible should be heated in an electric muffle furnace at 1100°. Gooch crucibles are less suitable because asbestos may be attacked by ammoniacal phosphate solutions. They may be employed if a blank shows that they do not undergo appreciable weight changes under the conditions of the determination.

Interfering substances. Before magnesium can be determined by precipitation as magnesium ammonium phosphate, it is necessary to remove all other metals possibly present, except the alkali

[1] J. I. Hoffman and G. E. F. Lundell, Bur. Standards J. Research *5*, 289 (1930).

[2] K. D. Jacob and D. S. Reynolds, J. Assoc. Official Agr. Chem. *11*, 128 (1928).

[3] S. J. Kiehl and H. B. Hardt, J. Am. Chem. Soc. *55*, 3555 (1933), have made some observations upon the ignition of magnesium ammonium phosphate. With reference to the blackening of the precipitate, they state: "The magnesium ammonium phosphate hexahydrate during the process of losing water of hydration in the early stages of the ignition possesses the property of attaching firmly within its complex structure certain gaseous organic compounds, if present, which later break down and leave graphitic carbon." They have shown that the luminescence which magnesium ammonium phosphate shows on ignition at 550°-600° is caused by the heat liberated in the conversion of amorphous magnesium pyrophosphate into a crystalline form. This crystallization may explain the great difficulty or impossibility of oxidizing the carbon by long heating at high temperatures. It seems highly probable that the crystallization of the pyrophosphate would result in the inclusion of the particles of carbon in the crystals, which then would be protected from the action of the oxygen of the air.

metals, because the former are precipitated in ammoniacal phosphate solution. In the regular course of analysis, magnesium will remain with calcium and the alkalies after the other metals have been separated with hydrogen sulfide and ammonium hydroxide. Calcium is separated from magnesium by precipitation as calcium oxalate (Chapter XXI).[1] Magnesium is thus finally left with the alkali metals, together with large amounts of ammonium salts which have accumulated in the course of the separations. The alkali metals are all coprecipitated to a greater or less extent with magnesium ammonium phosphate. Lithium forms a sparingly soluble phosphate. In the case of sodium the amount of coprecipitation is not large, and a precipitate virtually free from the metal can be obtained by a reprecipitation provided that excessive amounts are not present.[2] Potassium shows a much greater tendency to contaminate the precipitate, owing to the formation of mixed crystals of $Mg(NH_4,K)PO_4$. Triple precipitations may be required to yield a pure precipitate when large amounts of potassium are present. The unfavorable effect of large quantities of ammonium salts has already been noted; a double precipitation of magnesium ammonium phosphate under the proper conditions as already described gives a pure precipitate in their presence.

High concentrations of oxalate render the precipitation of magnesium ammonium phosphate incomplete, owing to the formation of complex magnesium-oxalate ions. Quantities of ammonium oxalate of the order of 1 g. in 100 to 200 ml. do not interfere sensibly. Sulfates in moderate concentrations and small amounts of citrates are without effect.

Determination of magnesium by the pyrophosphate method. The following directions apply to the determination of magnesium in a solution free from the interfering substances mentioned in the preceding section.

Procedure.

Reagent: Diammonium phosphate solution. Dissolve 25 g. of $(NH_4)_2HPO_4$ in 100 ml. of water.

Prepare duplicate neutral or slightly acid solutions of sample containing not more than 0.1 g. of magnesium oxide. Proceed with each solution as follows. Add 5 ml. of concentrated hydrochloric acid, and dilute to a total volume of approximately 150 ml. Add 10 ml. of freshly prepared ammonium phosphate reagent and a few drops of methyl red indicator to the solution, which should be at room temperature or preferably lower (cool in ice). Now add pure concentrated ammonium hydroxide slowly with constant stirring until the indicator turns pure yellow. Avoid scratching the sides of the beaker with the stirring rod. Continue to stir the solution for a few minutes, adding ammonia dropwise to keep the solution yellow, then add 5 ml. of concentrated ammonium hydroxide in excess, and stir again for a minute or two. Set the solution aside in a cool place for at least four hours, or preferably overnight.

---

[1] A very small amount of calcium remains in solution after precipitation with oxalate and is later precipitated with magnesium. It can be recovered from the weighed magnesium pyrophosphate as described on page 746.

[2] It is best not to use sodium phosphate or sodium ammonium hydrogen phosphate as a precipitant, although if only a slight excess of either is used in the second precipitation of magnesium ammonium phosphate correct results are usually obtained.

Filter through a retentive paper, and wash the precipitate moderately with cold 1 : 20 ammonium hydroxide solution. Dissolve the precipitate in approximately 50 ml. of warm 1 : 10 hydrochloric acid and wash the paper well with hot 1 : 100 hydrochloric acid solution. Dilute the solution to 150 ml., add 0.5 ml. of ammonium phosphate reagent, and cool to room temperature or, better, in ice. Then again precipitate magnesium by the addition of ammonium hydroxide as described above, and allow the solution to stand for at least four hours or, better, overnight. Filter through paper or a porcelain filter crucible, and wash the precipitate with cold 1 : 20 ammonium hydroxide until the washings, acidified with nitric acid, give no test for chloride ion with silver nitrate.

If a filter paper was used to collect the precipitate, fold it up, and place it in a weighed porcelain or platinum crucible. Char the paper, burn off the carbon at as low a temperature as possible with free access of air, and then ignite to constant weight at 1100° in an electric muffle furnace or, less preferably, over a Tirrill burner if a platinum crucible is used or over a Meker burner if a porcelain crucible is employed.[1] If a porcelain filter crucible is used, dry it first in an oven or over a low flame, and then heat gradually to 1100° in an electric muffle; if a furnace is not available, place the filter crucible inside an ordinary porcelain crucible, and heat gradually to the full heat of a Meker burner. Heat for half-hour periods until constant weight is obtained. Calculate the percentage of magnesium or magnesium oxide as required.

---

[1] If a black residue should be obtained, the oxidation of carbon will be aided if the crucible is cooled at intervals during the ignition to permit the entrance of air.

Other applications. Manganese, cadmium, zinc, cobalt, and other divalent metals as well, form double ammonium phosphates analogous to magnesium ammonium phosphate and can be determined by precipitation in this form under the proper conditions. Manganese ammonium phosphate is insoluble in excess ammonia, but the double phosphates of cadmium, zinc, and cobalt are soluble in ammoniacal solutions as a consequence of the formation of metal ammonio complexes. Therefore the latter metal ammonium phosphates must be precipitated in approximately neutral solutions and the precipitates washed with water. Fortunately, the double phosphates of the metals named are less soluble than magnesium ammonium phosphate, so that washing with water does not lead to any appreciable solubility loss. For zinc ammonium phosphate the optimum pH of precipitation is 6.6[1] (compare Fig. 71).

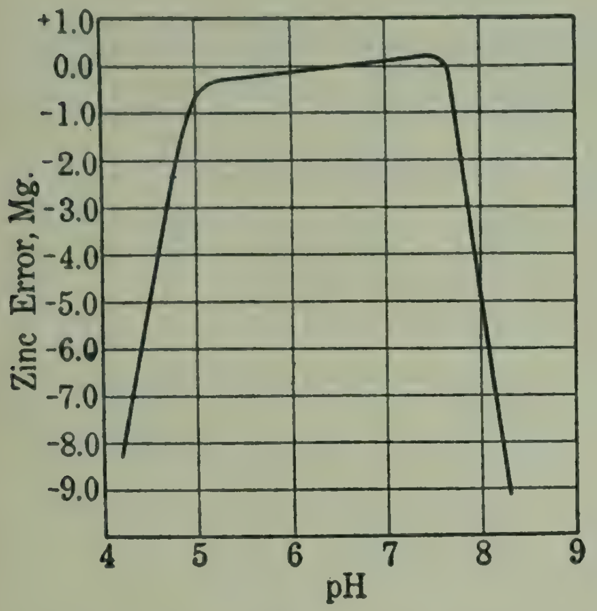


FIG. 71. Effect of pH on solubility loss in precipitation of $ZnNH_4PO_4$ (Ball and Agruss).

Phosphorus in the form of orthophosphate can be precipitated as magnesium ammonium phosphate with an excess of magnesium chloride in solutions containing ammonia and ammonium salts, and weighed as magnesium pyrophosphate (Chapter XXIV).

II. Determination of magnesium by precipitation as magnesium hydroxyquinolate.

Magnesium can be precipitated quantitatively with 8-hydroxyquinoline (oxine)[2] in the pH range 9.5 to about 13.[3] The precipitation is best made by adding the oxine solution to the ammoniacal magnesium solution containing ammonium salt.[4] There is a tendency for oxine to be carried down with the precipitate, and any large excess of reagent must be avoided. The precipitate has the composition $Mg(C_9H_6ON)_2 \cdot 2\ H_2O$ after drying at 105°. It rapidly becomes anhydrous when heated at 160°, but a slight decomposition takes place at this temperature.[4] The precipitate is preferably dried at 105°, although if it is contaminated with oxine better results are obtained by drying at 160° because most of the oxine is volatilized at this temperature.

---

[1] T. R. Ball and M. S. Agruss, J. Am. Chem. Soc. *52*, 120 (1930).

[2] R. Berg, Z. anal. Chem. *71*, 23 (1927); F. L. Hahn and K. Vieweg, Z. anal. Chem. *71*, 122 (1927); J. C. Redmond and H. A. Bright, J. Res. Bur. Stand. *15*, 113 (1936).

[3] H. R. Fleck and A. M. Ward, Analyst *58*, 388 (1933).

[4] C. C. Miller and I. C. McLennan, J. Chem. Soc. *1940*, 656. See also R. C. Chirnside, C. F. Pritchard, and H. P. Rooksby, Analyst *66*, 399 (1941).

The precipitation of magnesium as the quinolate requires the absence of all other metals save the alkalies, for nearly all of these yield slightly soluble hydroxyquinolates in ammoniacal solution. Small amounts of calcium are permissible, but usually when this metal is present double precipitations must be made, or, better, calcium should first be precipitated as the oxalate. A large excess of oxalate should be avoided in the calcium separation, for otherwise the precipitation of magnesium as quinolate may not be quantitative. In the presence of large amounts of the alkali metals, a double precipitation should be made.

The hydroxyquinolate method has a number of advantages over the classical phosphate method for magnesium. The advantage in drying the precipitate to constant weight at a low temperature instead of igniting at a high temperature, and the great rapidity of the new method are especially noteworthy. By the use of 8-hydroxyquinoline, magnesium can be separated from the alkali metals without the introduction of a nonvolatile reagent, which is a great advantage when the alkalies are to be determined (p. 748).

The following directions are essentially those of Miller and McLennan.[1]

Procedure. To 100 ml. of solution containing the equivalent of 0.01–0.05 g. of magnesium oxide, add 2 g. of ammonium chloride, 0.5 ml. of 0.02 per cent *o*-cresolphthalein in alcohol, and 6 N ammonium hydroxide in 2 to 3 ml. excess of that required to give a violet color (pH 9.5). Heat the solution to 70° or 80°, and add dropwise with stirring a 5 per cent solution of 8-hydroxyquinoline in 2 N acetic acid until a small excess is present as shown by a yellow color in the supernatant liquid. Digest for about half an hour on the steam bath, and then filter the hot solution through a weighed filter crucible. A trace of sodium tauroglycocholate in the solution reduces the tendency of the precipitate to stick to the beaker. Wash with about 50 ml. of warm water, and dry the precipitate at 105°–110°, first for an hour and then for one-half hour periods until constant weight is attained. The dried precipitate contains 2 molecules of water of hydration.

If too large an excess of oxine (100 per cent) was added, dry to constant weight at 160° and weigh as the anhydrous hydroxyquinolate.

PROBLEMS

1. What weight of sample must be taken in order that each milligram of $Mg_2P_2O_7$ residue shall represent 0.05 per cent MgO? *Ans.* 0.724 g.

2. If the solubility of $MgNH_4PO_4 \cdot 6\,H_2O$ in water is 0.11 g. per liter at 23°, how many milligrams of Mg and P_2O_5 does the saturated solution contain per liter? *Ans.* 10.9 mg. Mg; 31.8 mg. P_2O_5.

3. What volume of oxine solution containing 5 g. oxine per 100 ml. is required to precipitate 0.05 g. MgO?

---

[1] C. C. Miller and I. C. McLennan, J. Chem. Soc. *1940*, 656. See also R. C Chirnside, C. F. Pritchard, and H. P. Rooksby, Analyst *66*, 399 (1941).

4. A precipitate of magnesium ammonium phosphate has 1 per cent of the ammonium replaced by the equivalent amount of potassium. What will be the error when it is assumed that the precipitate is pure magnesium ammonium phosphate hexahydrate and (a) it is weighed as the hexahydrate after drying at room temperature, (b) it is ignited to 1100° and the residue weighed?

Ans. (a) $+ 0.09$ per cent; (b) $+ 0.42$ per cent.

5. 25.00 ml. of a magnesium chloride solution gave 0.5628 g. of $Mg_2P_2O_7$. What is the molarity of the solution?

CHAPTER XXIII

ANALYSIS OF LIMESTONE

By *limestone* is understood a carbonate rock consisting chiefly of calcium carbonate. A magnesian or dolomitic limestone is one containing considerable amounts of magnesium carbonate. *Dolomite* is strictly the equimolecular compound of calcium and magnesium carbonates, $CaCO_3 \cdot MgCO_3$, but the name is commonly applied to all carbonate rocks that contain sufficient magnesium carbonate to approach this composition more or less closely. It is, of course, impossible to differentiate sharply between these varieties. There exists an unbroken series of carbonates ranging

TABLE LVI. COMPOSITE ANALYSIS OF LIMESTONES[1]

	A	B
	%	%
SiO_2	5.19	14.09
TiO_2	0.06	0.08
Al_2O_3	0.81	1.75
Fe_2O_3 FeO	0.54	0.77
MnO	0.05	0.03
CaO	42.61	40.60
MgO	7.90	4.49
K_2O	0.33	0.58
Na_2O	0.05	0.62
Li_2O	Trace	Trace
$H_2O - (< 110°)$	0.21	0.30
$H_2O + (> 110°)$	0.56[a]	0.88[a]
P_2O_5	0.04	0.42
CO_2	41.58	35.58
S	0.09	0.07
SO_3	0.05	0.07
Cl	0.02	0.01
Organic	....	....
	100.09	100.34

[a] Includes organic matter.

---

[1] F. W. Clarke, *Data of Geochemistry*, U. S. Geol. Survey Bull. 770, 5th ed. (1924), p. 564. Column A, composite analyses of 345 limestones by H. N. Stokes; Column B, composite analyses by H. N. Stokes of 498 limestones used for building purposes.

from $CaCO_3$ to $CaCO_3 \cdot MgCO_3$. The procedure given below applies to the analysis of any of these varieties.

The minor constituents of limestone include the carbonates of ferrous iron, manganese, etc., as well as calcium sulfate, silicates, silica, iron pyrites, carbonaceous matter, and, of course, water. The composite analyses of a large number of limestones given in Table LVI serve to indicate the amounts of the subsidiary constituents to be found in the rock.

Limestone and dolomite have many technological uses and are therefore of great commercial importance. For judging the suitability of a limestone for a given technical purpose, a complete analysis is never required.[1] The following determinations are usually made in a shorter technical analysis:

I. Loss on ignition
II. Silica
III. Combined oxides, "R_2O_3." This is the residue obtained by igniting the precipitate formed by ammonium hydroxide. It consists of Al_2O_3, Fe_2O_3, TiO_2, Mn_3O_4, and P_2O_5, the latter combined as aluminum, iron, or titanium phosphate
IV. Calcium oxide
V. Magnesium oxide
VI. Carbon dioxide.

Plan of procedure.

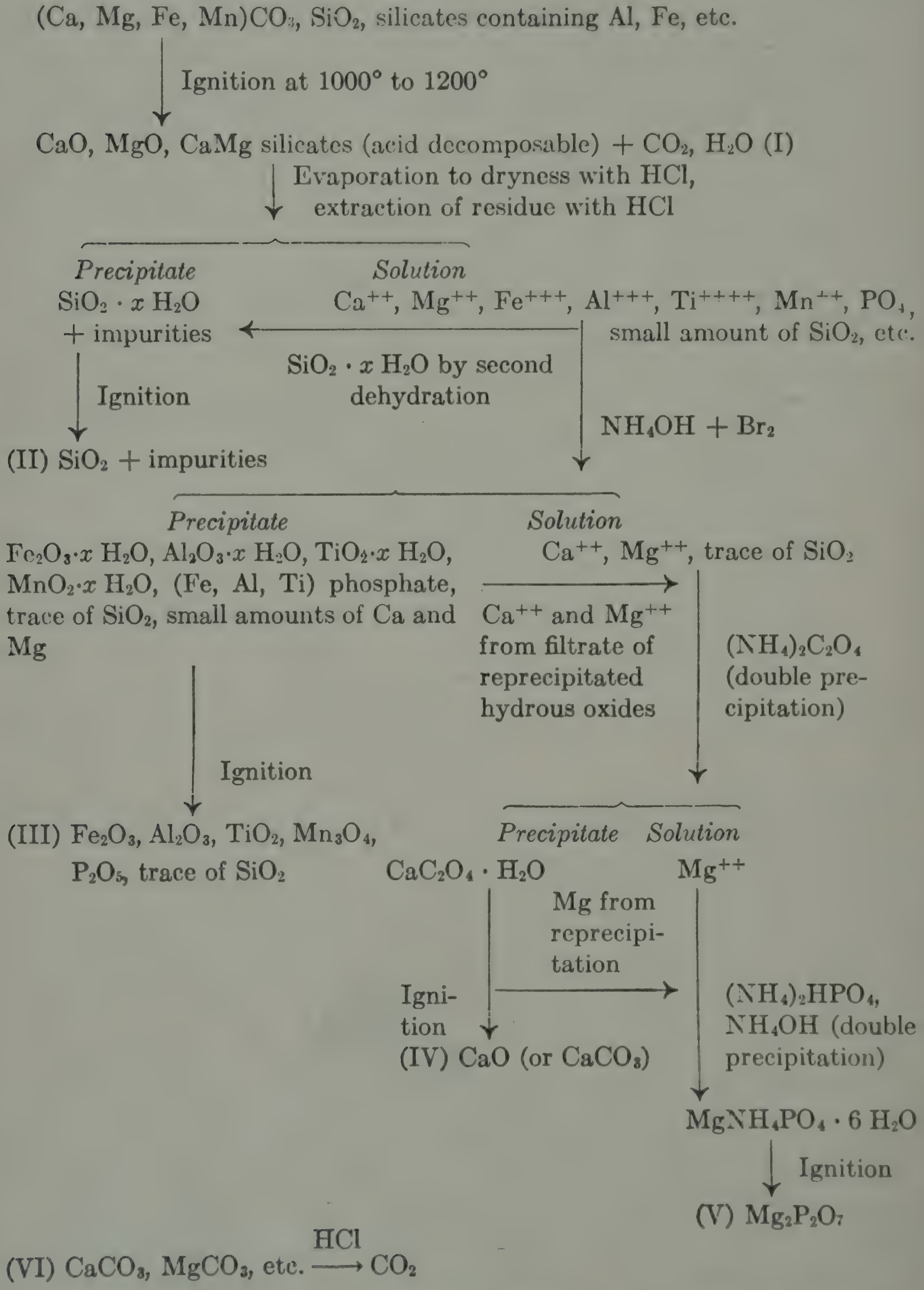
The diagrammatic outline on page 378 serves to indicate the procedure followed in a "proximate" analysis of limestone for the determination of loss on ignition (I), silica (II), combined oxides of iron, aluminum, etc. (III), calcium (IV), magnesium (V), and carbon dioxide (VI).

I. Loss on ignition.

When heated at moderately elevated temperatures (1000° to 1100°), a limestone loses all of its carbon dioxide and moisture, and any carbonaceous matter present is oxidized. At the same time reactions may occur which lead to an increase in weight, as, for example, oxidation of sulfides to sulfates and of ferrous iron and manganese. At a higher temperature ($> 1200°$) sulfur will be lost as the result of decomposition of sulfates, and the alkalies will be volatilized. The ignition loss represents approximately the amount of carbon dioxide (and water) in the sample.

---

[1] For refined methods of carbonate rock analysis, such as are needed for scientific purposes, see W. F. Hillebrand, *Analysis of Silicate and Carbonate Rocks*, U. S. Geol. Survey Bull. 700 (1919), p. 246; Hillebrand and Lundell, *Applied Inorganic Analysis*, p. 819.


(Ca, Mg, Fe, Mn)CO_3, SiO_2, silicates containing Al, Fe, etc.
Ignition at 1000° to 1200°
CaO, MgO, CaMg silicates (acid decomposable) + CO_2, H_2O (I)
Evaporation to dryness with HCl, extraction of residue with HCl
Precipitate
$SiO_2 \cdot x\,H_2O$ + impurities
Solution
Ca^{++}, Mg^{++}, Fe^{+++}, Al^{+++}, Ti^{++++}, Mn^{++}, PO_4, small amount of SiO_2, etc.
$SiO_2 \cdot x\,H_2O$ by second dehydration
Ignition
(II) SiO_2 + impurities
$NH_4OH + Br_2$
Precipitate
$Fe_2O_3 \cdot x\,H_2O$, $Al_2O_3 \cdot x\,H_2O$, $TiO_2 \cdot x\,H_2O$, $MnO_2 \cdot x\,H_2O$, (Fe, Al, Ti) phosphate, trace of SiO_2, small amounts of Ca and Mg
Solution
Ca^{++}, Mg^{++}, trace of SiO_2
Ca^{++} and Mg^{++} from filtrate of reprecipitated hydrous oxides
$(NH_4)_2C_2O_4$ (double precipitation)
Ignition
(III) Fe_2O_3, Al_2O_3, TiO_2, Mn_3O_4, P_2O_5, trace of SiO_2
Precipitate
Solution
$CaC_2O_4 \cdot H_2O$
Mg^{++}
Mg from reprecipitation
Ignition
(IV) CaO (or $CaCO_3$)
$(NH_4)_2HPO_4$, NH_4OH (double precipitation)
$MgNH_4PO_4 \cdot 6\,H_2O$
Ignition
(V) $Mg_2P_2O_7$
(VI) $CaCO_3$, $MgCO_3$, etc. $\xrightarrow{HCl}$ CO_2

Procedure. Weigh 0.5 g. of ground air-dry sample into a covered crucible (porcelain will do, but platinum is better) and dry at 110° for one hour. Cool and weigh. The loss in weight represents hygroscopic moisture. Then ignite the crucible and its contents strongly, preferably in an electric furnace regulated to 1000° to 1100°, or over a Meker burner. The heating should be slow at first to prevent mechanical loss through sudden expulsion of carbon dioxide. Heat for one-half to one hour, cool, and weigh. Repeat the ignition to constant weight, using half-hour periods of heating. Remember that the ignited residue is hygroscopic. Calculate the loss on ignition in per cent.

II. Silica.

After the ignition of I, the sample is in the proper condition for the determination of silica. Any acid-insoluble silicates originally present will have been converted into acid-decomposable calcium magnesium silicates by the intense heating with calcium oxide. The ignition residue is treated with excess hydrochloric acid, and the solution is evaporated to dryness to dehydrate the silica and render it insoluble as described in Chapter XXV. Unless the amount of silica present is small, two dehydrations of silica with intervening filtration should be made to separate as much of it as possible. As stated in the chapter on Silica, a small amount of silica escapes separation even after two evaporations, but no account is taken of this trace in the technical analysis of limestone. When the silica that escapes separation after the second dehydration is not recovered, as is the case here, the ignited silica should not be corrected for the impurities present by hydrofluorizing (p. 405), because the two errors will compensate each other to a certain extent.[1]

Procedure. Transfer the residue of the ignition of (I) to a small covered casserole, add 5 ml. of water, and clean the crucible with a few drops of dilute hydrochloric acid, adding the solution to the casserole. Add 5 ml. of concentrated hydrochloric acid to the casserole, and hasten solution of the residue by disintegration with a glass rod. Evaporate the solution to dryness on the steam bath, and heat the residue for one-half to one hour at 100° to 110°. Pour 5 ml. of concentrated hydrochloric acid over the residue, and allow the mixture to stand for two to three minutes. Then add 25 ml. of water, and heat on the steam bath for five to ten minutes to bring all soluble material into solution, using a stirring rod to break up any lumps present. Filter off the silica on quantitative paper; wash the precipitate thoroughly with 1 : 100 hydrochloric acid and finally once or twice with water to remove most of the hydrochloric acid. Evaporate the filtrate and washings to dryness in the original casserole, heat the residue at 100° to 110°, and then take it up in hydrochloric acid and digest as before, using, however, smaller volumes of acid and water the second time. Filter off the second portion of silica on a fresh small filter paper, and wash as before with 1 : 100 hydrochloric acid and finally with one or two portions of water. Reserve the combined filtrates and washings for III. Place the two silica precipitates in a weighed crucible and ignite to SiO_2 over a Meker burner (p. 409). Report the percentage of SiO_2 present.

---

[1] The following data given by Hillebrand and Lundell, *Applied Inorganic Analysis*, p. 844, are of interest in this connection. The percentage of silica in an argillaceous limestone containing 18.08 per cent of SiO_2 as obtained by a *single* evaporation was 17.80 per cent when no corrections were made, 17.71 per cent when the residue was hydrofluorized, and 17.90 per cent when the preceding result was corrected for the silica in the ammonium hydroxide precipitate.

NOTES:

1. If the limestone is very impure, i.e., contains much silicate, it is best to ignite strongly the finely powdered sample in a platinum crucible with half its weight of anhydrous sodium carbonate and then to treat the product with an excess of hydrochloric acid as above.

2. Perchloric acid can be used to advantage in the dehydration of silica in this determination.[1]

III. Combined oxides (Fe_2O_3, Al_2O_3, TiO_2, Mn_3O_4, and P_2O_5).

By adding a slight excess of ammonium hydroxide to the filtrate from the silica, there is obtained a precipitate of the hydrous oxides of ferric iron, aluminum, titanium, and of phosphorus (as the phosphates of these metals). In order to precipitate manganese quantitatively, it is necessary to add an oxidizing agent such as bromine, ammonium persulfate, or hydrogen peroxide to oxidize the element to the quadrivalent state, in which form it is precipitated by ammonium hydroxide as hydrous manganese dioxide. The use of ammonium persulfate is open to the objection that sulfate is introduced into the solution and later may give rise to the coprecipitation of calcium sulfate with calcium oxalate. Bromine water is free from these objections, but it is a little difficult to precipitate manganese quantitatively by its use. The oxidation of manganese is carried out in a weakly ammoniacal solution. Bromine reacts with ammonium ion in weakly acid or basic solutions:

$$2\,NH_4^+ + 3\,Br_2 \rightarrow 8\,H^+ + N_2 + 6\,Br^-,$$

---

[1] F. H. Fish and F. M. Taylor, J. Chem. Educ. *10*, 246 (1933).

and the excess added is thus quite rapidly destroyed. As a consequence the oxidation and precipitation of manganese may be incomplete. However, it seems that for the small quantities of manganese usually present in limestones fairly satisfactory results are obtained by the use of bromine.[1]

Any large excess of ammonium hydroxide must be avoided in the precipitation, or else aluminum may be incompletely precipitated (p. 325). Magnesium and calcium hydroxides are coprecipitated to a small extent with the hydrous oxides (p. 320). Moreover, calcium carbonate may possibly be precipitated to a slight extent by the ammonium carbonate formed when the ammoniacal solution is exposed to the atmosphere or by that originally present in the ammonium hydroxide. For these reasons the ammonia precipitate is dissolved in hydrochloric acid and again precipitated. The first and second filtrates are combined and reserved for the determination of calcium and magnesium.

Any silica in solution at the time of the ammonia precipitation will be partially precipitated with the hydrous oxides. It should be realized that small amounts of iron, titanium, etc. are retained in the main silica precipitate as impurities and thus escape determination in the procedure given; the error is very small.

Procedure. Heat the filtrate from II (having a volume of 150 to 200 ml.) nearly to boiling, add pure concentrated ammonium hydroxide slowly until a slight precipitate appears, and then add 5 ml. of fresh saturated bromine water. Add ammonium hydroxide dropwise with stirring until a slight excess is present as indicated by litmus paper. Allow the liquid to stand for five or ten minutes near the boiling point, and then filter through a small rapid quantitative paper. Wash the precipitate three or four times with hot 1 per cent ammonium chloride solution. Test the filtrate with ammonium hydroxide for complete precipitation. Dissolve the precipitate in 10 ml. or so of hot 1 : 1 hydrochloric acid, and receive the solution in the original beaker. Wash the filter paper thoroughly with hot water. Dilute the solution to 75 ml., and precipitate the hydrous oxides as before, again using 5 ml. of bromine water. Filter, catching the filtrate in the beaker containing the filtrate from the first precipitation. Wash the precipitate thoroughly with 1 per cent ammonium chloride solution. Place the damp paper in a weighed crucible, char, burn off the carbon at a low temperature, and then ignite strongly (p. 322). Report the percentage of mixed oxides ("R_2O_3").[1]

---

[1] E. V. Holt and H. F. Harwood, Mineral Mag. *21*, 318 (1928), investigated the use of ammonium persulfate, hydrogen peroxide, chlorine, and bromine for the oxidation of manganese in rock analysis and found bromine to be the most satisfactory for the purpose.

IV. Calcium.

The filtrate from the hydrous oxide precipitation will contain all of the calcium and magnesium, as well as the small amounts of sodium and potassium originally present in the sample. For the accurate determination of calcium in limestones, especially the dolomitic varieties, a double precipitation of calcium oxalate should be made (p. 355). However, results of fair accuracy, sometimes satisfactory for the purpose, can be obtained by making only one precipitation under the conditions recommended in Chapter XXI.

Procedure. Concentrate the filtrate and washings from III to 200 or 250 ml. after acidification with hydrochloric acid, and proceed as directed on p. 358. Report the percentage of calcium oxide present.

V. Magnesium.

The filtrate from the calcium precipitation will contain such large amounts of ammonium salts, and of the especially harmful oxalates, that it is advisable to destroy these in accurate work before precipitating magnesium as magnesium ammonium phosphate. This can be done most conveniently by oxidation with nitric acid in hot solution in the presence of chloride. Oxalate is thus oxidized to carbon dioxide and water, and ammonium ion to water, nitrous oxide, and nitrogen.

Procedure. Add 75 ml. of concentrated nitric acid to the combined filtrates and washings from IV, and evaporate to dryness on the steam bath. Only a small residue (of magnesium salts) should remain. Add 2 ml. of concentrated hydrochloric acid and 25 ml. of water, warm for a few minutes, and filter through a small paper if a slight residue of silica remains. Wash the paper carefully, and then determine magnesium in the filtrate as directed on p. 371. Report the percentage of magnesium oxide present.

Alternative method of decomposing limestones for the determination of calcium and magnesium. If it is desired to determine only calcium and magnesium in a limestone, the method of decomposition described in the next paragraph may often be used. In this method the calcium and magnesium present in acid-insoluble silicates occurring in the sample are not brought into solution, whereas in the ignition method described on p. 379 all the calcium and magnesium are rendered soluble.

---

[1] If it is desired to examine the ignited residue, follow the directions given on pp. 738 *et seq.* The oxides in the ignited silica should then be recovered and added to the main portion as described on p. 737.

Weigh 0.5 g. of finely ground sample into a 200 ml. casserole, cover with a watch glass, and add 5 ml. of water and then 10 ml. of 1 : 1 hydrochloric acid (in small portions at a time if there is vigorous effervescence). Evaporate to dryness on the steam bath, and heat the residue at 100° to 110° for one-half hour. Then add 25 ml. of 1 : 2 hydrochloric acid, and warm on the steam bath, with stirring, for ten minutes. Filter off the residue on paper, and wash thoroughly with 1 : 100 hydrochloric acid; the residue may be ignited, weighed, and reported as "insoluble material" or "gangue."

Heat the combined filtrate and washings nearly to boiling, add 5 ml. of saturated bromine water and then ammonium hydroxide in very slight excess (see p. 381). Allow the precipitate to settle for a few minutes and then filter. Wash the paper and precipitate a few times with hot 1 per cent ammonium chloride solution, allowing the washings to run into the filtrate. Place the precipitation beaker under the funnel, and pour a small volume of hot dilute hydrochloric acid over the paper to dissolve the precipitate. Wash the paper thoroughly with hot water. Reprecipitate the hydrous oxides as before with bromine and ammonium hydroxide. Filter through the same filter paper, and wash with ammonium chloride solution. Combine the filtrates and washings, and proceed as described under IV.

VI. Carbon dioxide.

The carbon dioxide content of a carbonate is determined by treating the sample with dilute hydrochloric or perchloric acid in a suitable apparatus and (1) finding the loss in weight due to the carbon dioxide liberated (indirect method) or (2) absorbing the carbon dioxide evolved in a suitable medium and ascertaining the gain in weight of the absorbent. The first method gives satisfactory results for samples containing relatively large amounts of carbon dioxide and is often used because of its simplicity and rapidity. The second method generally gives more accurate results but requires more elaborate apparatus.

1. ***Indirect method.*** For the indirect determination of carbon dioxide a compact apparatus called an alkalimeter (Fig. 72) is used. The alkalimeter is weighed after charging with sample and acid, the acid is allowed to react with the carbonate, and the apparatus is then weighed again after all the carbon dioxide has been expelled. Naturally the gas escaping from the reaction flask is saturated with water vapor, so that it must be passed over a drying agent, which removes and retains the moisture. To remove the carbon dioxide quantitatively from the solution and the free space of the apparatus, a current of dry air is drawn through the warm liquid

Procedure. First, see that the alkalimeter is clean and dry, inside and out. Place a wad of cotton in the bottom of *B* (Fig. 72), and fill this tube three-quarters full with one of the perchlorate driers (anhydrous magnesium perchlorate, magnesium perchlorate trihydrate, or barium perchlorate), anhydrous calcium sulfate, or, less preferably, granulated calcium chloride.[1] Place another plug of cotton at the top of the column of drier, and be sure that no particles of desiccant adhere to the tube above the cotton. Insert the top part of the tube, and close it for the time being with a short piece of rubber tubing closed at one end with a short section of glass rod (t_2). Also fill the two drying tubes T_1 and T_2, provided with tightly fitting one-hole rubber stoppers, with the same drying agent as used in *B*, placing small plugs of cotton in the ends of the tubes. Keep these tubes closed with short sections of rubber tubing stopped with glass rod when not in use. Next fill the tube *A* about two-thirds full[2] with 4 *N* perchloric acid or, less preferably, with 4 *N* hydrochloric acid; be sure that the stopcock is closed so that no acid will run into the flask *F*, and be careful to keep the ground-glass surfaces dry.

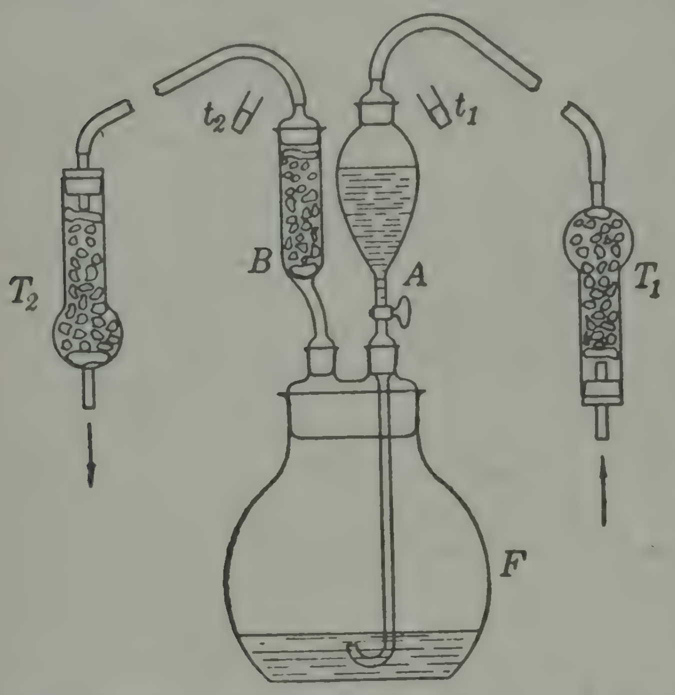


FIG. 72. Alkalimeter for indirect determination of carbon dioxide.

When all is in readiness, weigh 1.5 g. of powdered sample into the flask, and add a few ml. of water to moisten the powder. Replace the top of the flask, and stopper *B* and *A* with the tubes t_2 and t_1. Place the whole on the balance and weigh, preferably using another similar alkalimeter as a tare (p. 222). Be sure that the alkalimeter is at room temperature (do not warm it by injudicious handling) and that it is clean and dry on the outside. It is best to allow the apparatus to stand near the balance for a half-hour before weighing. The stopper t_2 should be removed momentarily before weighing to assure the same pressure inside the apparatus as outside.

---

[1] Anhydrous calcium chloride as purchased always contains small amounts of calcium hydroxide. The presence of the latter substance is, of course, very objectionable when calcium chloride is used to dry carbon dioxide as in this determination. Therefore the calcium chloride to be used for this purpose should be saturated with carbon dioxide previous to use by being allowed to stand overnight in an atmosphere of the gas, and the latter should then be washed out with dry air. Such treatment, however, does not guarantee the conversion of all hydroxide present into carbonate, so that on absorption of water during subsequent use, some of the unattacked hydroxide may become exposed. For this reason especially, the perchlorate driers are to be preferred.

[2] It is best to calculate the volume of acid required and to use an excess of, say, 50 per cent.

Remove the apparatus from the balance, attach the drying tubes T_1 and T_2 with short lengths of rubber tubing, and allow the acid in A to run slowly into the flask at such a rate that there is a brisk but not violent evolution of carbon dioxide. Allow the apparatus to stand at room temperature for fifteen minutes or until little or no carbon dioxide is being evolved. Then draw a slow current of air through the apparatus in the direction indicated in Figure 72, and heat to 80° or 90° but not to boiling. Remove the flame, and continue to draw air through the solution at the rate of two or three bubbles per second until it is cold. Disconnect the drying tubes, replace the plugs t_1 and t_2, place the alkalimeter (wiped off with a cloth if necessary) near the balance, and allow it to stand for one-half hour. Then weigh as before against the tare, momentarily removing the plug t_2 to equalize the pressure within the flask. From the decrease in weight calculate the percentage of carbon dioxide in the sample.

2. *Direct method.* In the direct method for carbon dioxide, matters must be so arranged that the gain in weight of the carbon dioxide absorbent actually represents the amount of carbon dioxide present in the sample, i.e., all the carbon dioxide must be liberated and absorbed, no other gases may be absorbed, and the absorbing medium must neither gain nor lose water. These requirements are met in the apparatus described below.

Apparatus. The form of apparatus illustrated in Figure 73 is suitable for use in an instructional laboratory.[1] It should be understood that minor modifications can be made in the train as far as form of the separate pieces is concerned.

The decomposition vessel A (Fig. 73) is a 200 or 250 ml. Erlenmeyer flask fitted with a two-hole rubber stopper through which pass a small condenser C and a dropping funnel B. The upper end of the dropping funnel is closed with a one-hole rubber stopper carrying a drying tube *D* filled with ascarite (sodium hydroxide-asbestos) resting on a small plug of cotton; the upper end of the drying tube is closed with a plug of cotton. The stem of the dropping funnel reaches nearly to the bottom of the flask and is bent upwards at its lower end to prevent the entrance of carbon dioxide. The upper end of the condenser is connected with the purification train by means of a short section of fresh gum tubing. In this, and other glass-to-glass connections, the two ends of the glass tubing should be in contact.

---

[1] For a slightly better form, in which connections are made by mercury seals instead of rubber tubing, and Wesson tubes are used in place of U-tubes as absorption vessels, see Hillebrand and Lundell, *Applied Inorganic Analysis*, p. 623.

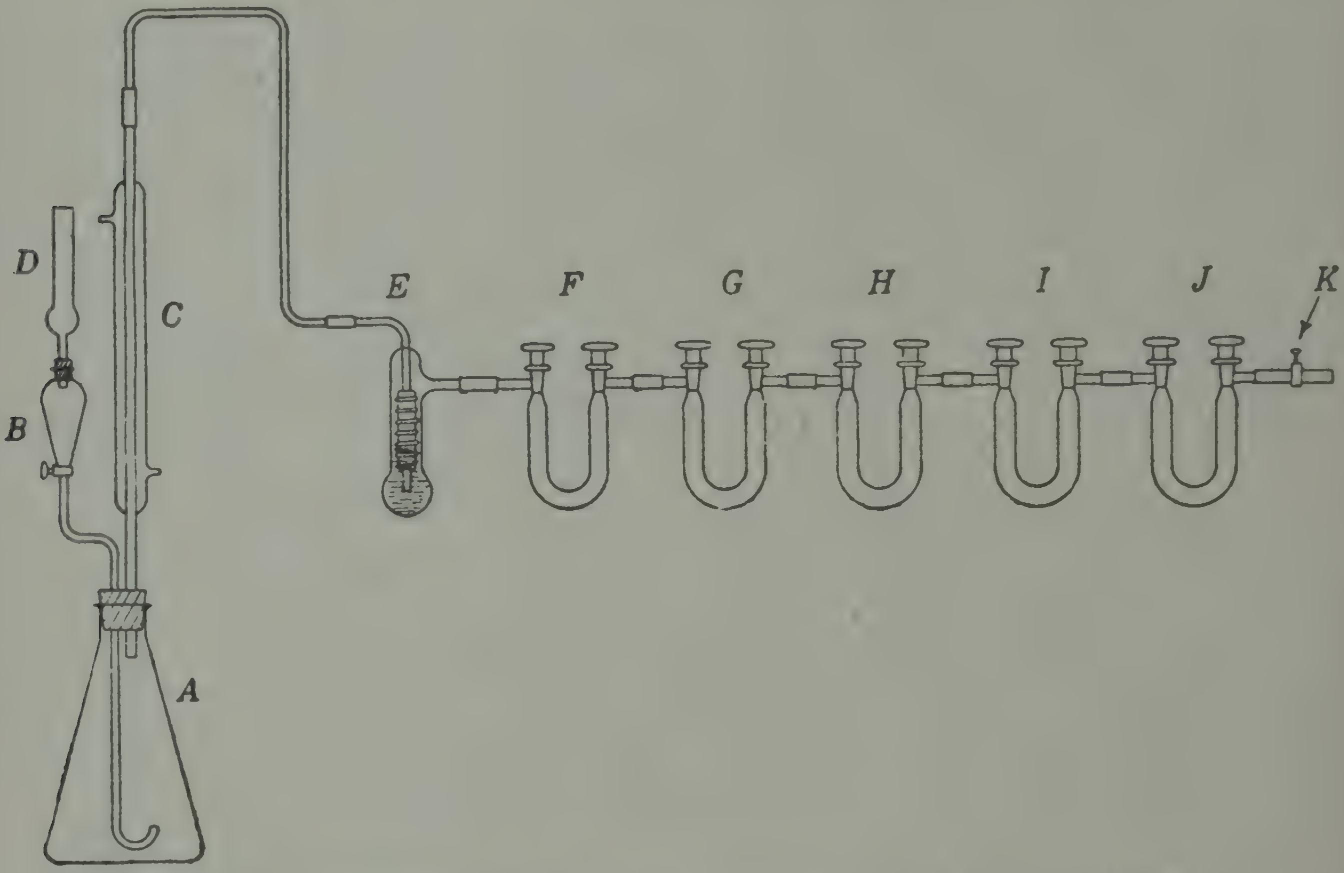


Fig. 73. Apparatus for direct determination of carbon dioxide.

The bottle *E* is partially filled with concentrated sulfuric acid, the function of which is to remove most of the water vapor from the entering gas. The U-tube *F* is filled with dehydrated copper sulfate in pumice,[1] which removes hydrogen sulfide and hydrochloric acid from the gas stream. The second U-tube *G* contains anhydrous magnesium perchlorate or magnesium perchlorate trihydrate,[2] which serves to remove the water vapor still remaining in the gas. The U-tubes *H* and *I* are the absorption vessels and are each filled two-thirds full of ascarite[3] and one-third full of magnesium perchlorate or magnesium perchlorate trihydrate, as shown in Figure 74 (the same desiccant must be used as is contained in *G*). The ascarite absorbs the carbon dioxide and, with the drying agent following, takes up the water formed in the reaction:

---

[1] The dehydrated copper sulfate-pumice is prepared by soaking pulverized pumice having the size of a grain of wheat in saturated copper sulfate solution and drying at 150° to 180°. The product must be kept in a well-stoppered bottle.

[2] If these are not procurable, anhydrous calcium chloride may be used. See footnote on p. 384 regarding calcium hydroxide in calcium chloride.

[3] If ascarite is not available, soda-lime may be used in *H*, *I*, and *D*.

$$2\,NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O.$$

Ascarite is not a particularly good drying agent, and it is therefore followed by a good desiccant to take up any water which may pass through. The use of two absorption tubes assures the complete absorption of carbon dioxide and gives an indication when the first tube must be recharged. The last tube *J* contains magnesium perchlorate (anhydrous or trihydrate) together with ascarite and serves the purpose of protecting the absorption tubes. From the last U-tube a rubber tube provided with a screw clamp *K* to regulate the flow leads to the suction line or an aspirator. All the U-tubes are hung by copper or brass wire from a horizontal iron rod, and the arrangement is made as compact as possible.

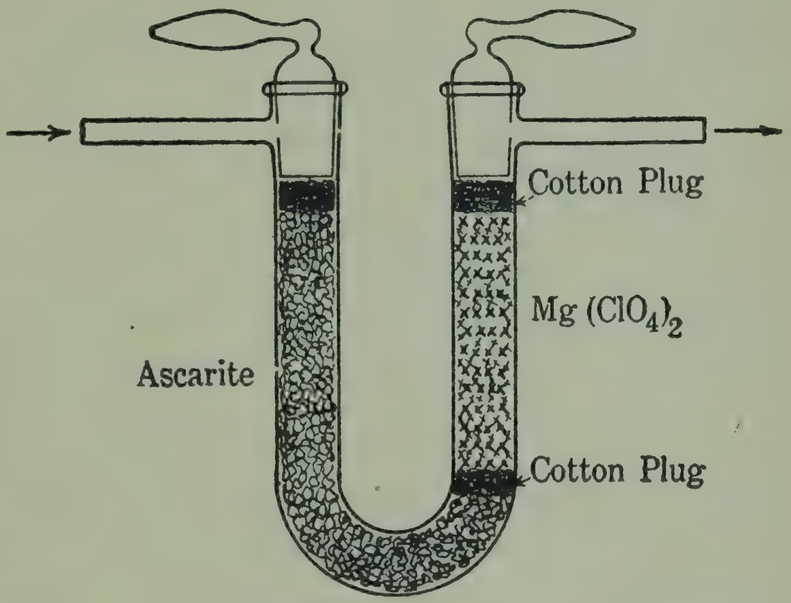


FIG. 74. Absorption tube for carbon dioxide.

Procedure. First test the apparatus for gas-tightness as follows. Pour enough water into the flask *A* to cover the lower end of the dropping funnel, replace the stopper, and close the top of the tube *D* tightly with a well-fitting stopper. Apply gentle suction, gradually open the clamp *K* until one bubble per second passes through *E*, and keep it open until the bubbles cease (which will occur if the apparatus is free from leaks). Close *K* tightly, and allow the apparatus to stand under the slight vacuum for five minutes. Then close the stopcock of *B*, remove the stopper, gradually open the stopcock of the funnel *B*, and note whether there is an inrush of air as denoted by bubbles in *A*. If the vacuum has been maintained, it may be assumed that the apparatus is free from significant leaks. If the apparatus is not found to be gas-tight, examine all the connections carefully, replace any that appear to be defective, wire the rubber tubing to the glass, and again test for leaks.[1]

When the train has been found to be gas-tight, draw a current of air through it at the rate of about two bubbles per second for fifteen minutes. Then close the stopcocks of the absorption tubes *H* and *I*, disconnect the tubes from the train, and weigh them separately against a similar U-tube used as a tare. Allow the tubes to stand in or near the balance case for one-half hour before weighing. Open a stopcock of each absorption tube and of the tare for an instant before weighing. Replace the absorption tubes in the train, and repeat the operation of drawing air through the system until the weight of each tube is constant to 0.5 mg.

When constant weight has been attained, weigh 1 to 1.5 g. of sample into the flask *A*, add 50 ml. of water or enough to cover the lower end of the dropping funnel, disconnect the absorption tubes and the protecting tube *J* from the train, attach the suction line connection to *G*, and draw a slow stream of air through the rest of the apparatus for five minutes to remove any carbon dioxide introduced in opening the flask *A* when weighing the sample. Then connect in the absorption tubes, leaving *K* open and the vacuum source disconnected. Pour 50 ml. of 1 : 1 hydrochloric acid into the funnel *B*, replace the ascarite tube *D*, and then allow the acid to flow slowly into the flask so that there is a slow evolution of carbon dioxide, corresponding to the passage of about three bubbles per second through *E*. When all of the acid has been added and only a slow evolution of carbon dioxide is taking place, close the stopcock of *B*, start the water circulating in the condenser *C*, and gradually heat the contents of the flask to boiling. Connect the train to the suction line, open the stopcock of *B*, and regulate *K* so that approximately two bubbles of gas per second pass through the train. Continue the boiling gently for a few minutes, and then gradually reduce the heat, finally taking away the source altogether. In the meantime regulate the suction so that a constant slow stream of carbon dioxide-free air is being drawn through the system. Continue to draw air through the apparatus for twenty to thirty minutes after the cessation of heating. Reweigh the absorption tubes against the tare, taking the same precautions as in the first weighing. Repeat the determination until satisfactory checks are obtained. Report the percentage of carbon dioxide obtained.

---

[1] In careful work it is desirable to test the apparatus by determining the carbon dioxide content of a sample containing a known amount of carbonate (anhydrous sodium carbonate for standardization — see p. 547 — may be used).

PROBLEMS

1. Assuming a sample of limestone to consist entirely of $CaCO_3$, calculate:

(a) The volume of 4 *N* hydrochloric acid required to liberate all the carbon dioxide from a 1 g. sample.

(b) The volume of carbon dioxide obtained in (a) measured at 21° C. and 745 mm. of mercury.

(c) The volume of ammonium oxalate solution containing 4.0 g. $(NH_4)_2C_2O_4 \cdot H_2O$ in 100 ml. of solution required to precipitate the calcium in a 1 g. sample.

Ans. (a) 5.00 ml.; (b) 246.0 ml.; (c) 35.5 ml.

2. A sample consisting only of calcium and magnesium carbonates is found to contain 20.0 per cent of calcium. Find the percentage of magnesium in the material. *Ans.* 14.41 per cent.

3. A 0.6033 g. sample of air-dry limestone containing negligible amounts of silica, iron, aluminum, etc., gave a loss of 0.0022 g. on heating to 110°, and a further loss of 0.2710 g. after strong ignition. Calculate the approximate molar ratio of magnesium to calcium in the limestone. Explain why the calculated result can be only approximate at best. *Ans.* 0.20.

4. A mixture consisting only of calcium carbonate, magnesium carbonate, and calcium sulfate is found to contain 25.0 per cent of carbon dioxide and 27.0 per cent of calcium. Calculate the percentage of calcium and magnesium carbonates and calcium sulfate.

Ans. 32.94 per cent $CaCO_3$; 20.16 per cent $MgCO_3$; 46.90 per cent $CaSO_4$.

5. Deduce the formula of a mineral having the following percentage composition, counting the iron with magnesium (isomorphous replacement): CaO, 30.40; MgO, 14.66; FeO, 9.30; CO_2, 45.60.

CHAPTER XXIV

DETERMINATION OF PHOSPHORUS

Method.

In the absence of interfering elements, phosphorus (in the form of orthophosphate) is precipitated as magnesium ammonium phosphate hexahydrate by magnesium chloride and ammonium chloride in ammoniacal solution:

$$PO_4^{\equiv} + NH_4^+ + Mg^{++} + 6\,H_2O \underset{\textit{(ammoniacal solution)}}{\longrightarrow} MgNH_4PO_4 \cdot 6\,H_2O.$$

The precipitate is ignited to magnesium pyrophosphate and weighed as such:

$$2(MgNH_4PO_4 \cdot 6\,H_2O) \rightarrow Mg_2P_2O_7 + 2\,NH_3 + 13\,H_2O.$$

When interfering substances such as calcium, iron, etc., which would otherwise be precipitated, are present, two courses are open:

(1) The precipitation of magnesium ammonium phosphate may be made in the presence of much ammonium citrate, which prevents the precipitation of calcium and other phosphates. This procedure may be applied in the analysis of samples high in phosphorus (phosphate rock).

(2) Phosphorus may first be separated from the interfering elements by precipitation as ammonium phosphomolybdate in acid medium. This precipitate may then be dissolved in ammonia, and magnesium ammonium phosphate precipitated. This procedure is used for samples that are low in phosphorus.

Solution of sample.

Material attacked by mineral acids is decomposed with nitric acid if separation of phosphorus as ammonium phosphomolybdate is to follow. Other mineral acids are avoided, because they will interfere in the precipitation of ammonium phosphomolybdate; if their use is required in the decomposition of the sample, as small an amount as possible is employed, and the excess is removed by evaporation.[1]

---

[1] Sulfuric acid cannot be removed by volatilization, because at the high temperature necessary phosphorus is lost.

Acid-insoluble material is treated with hydrofluoric acid (see p. 755) or fused with sodium carbonate. In the latter case, leaching of the melt with water extracts the phosphate. Silicic acid is removed by dehydration in the usual manner (p. 402) before proceeding further in the analysis. If titanium, tin, or other metals forming phosphates slightly soluble in acids are present, the corresponding phosphates will be left with the silica if the sample is decomposed with acids, and steps must be taken to recover such phosphorus.[1]

Metallurgical products contain phosphorus mostly in the form of phosphide, and an oxidizing attack is required to convert the latter into orthophosphate and prevent loss of phosphorus as phosphine (see p. 713).

Precipitation of ammonium phosphomolybdate.

When a nitric acid solution of ammonium molybdate is added to a solution containing orthophosphate ion, there is formed a yellow precipitate of ammonium phosphomolybdate having a composition approaching that represented by the formula $(NH_4)_3PO_4 \cdot 12\,MoO_3 \cdot 2\,HNO_3 \cdot H_2O$. The composition depends upon such factors as the composition of the reagent used, the presence of other substances in solution, and especially upon the temperature of precipitation. When the precipitation is made below 50°, the composition of the precipitate closely approximates the formula given. In the gravimetric procedure in which phosphorus is finally precipitated as magnesium ammonium phosphate, it matters but little what the composition of the yellow precipitate is, as long as all the phosphorus is precipitated. In other methods, especially the volumetric (p. 716), it is very important that the precipitate correspond to the formula given, at least as far as the ratio of phosphorus to molybdic oxide is concerned, if the theoretical factor is to be used. In the volumetric methods the calculations are based on the assumption that the ratio $PO_4 : MoO_3 = 1 : 12$ holds for the precipitate obtained, and then the directions for obtaining such a precipitate must be carefully followed.

The precipitation of ammonium phosphomolybdate is carried out in nitric acid solution, hydrochloric and sulfuric acids being avoided as far as possible owing to the greater solubility of the precipitate in their presence. It is important to have present a rather large amount (5 to 15 per cent) of ammonium nitrate. This salt hastens the separation of the precipitate and decreases its solubility as a result of the common-ion effect. At concentrations above approximately 15 per cent of ammonium nitrate, the solubility of the yellow precipitate is increased. A large excess of ammonium molybdate reagent is required for successful precipitation. Precipitation is much more rapid in warm than in cold solutions, and precipitates formed at higher temperatures are easier to filter. However, precipitates formed above 50° contain more molybdic oxide than corresponds to the ideal formula given above. In warm solutions all of the phosphorus is probably precipitated within one-half hour if the solution is stirred and substances retarding precipitation are absent, but it is best to allow the precipitation mixture to stand overnight (at room temperature). Precipitation at room temperature is complete within ten hours. Unless substances are present which contaminate the precipitate when formed in warm solutions, the precipitation is always made warm. The precipitate must be washed with a solution of an electrolyte; pure water peptizes the precipitate and causes it to run through the filter. A dilute solution of ammonium nitrate is a suitable wash liquid if phosphorus is to be precipitated later as magnesium ammonium phosphate. If the precipitate is to be titrated (p. 716), a solution of potassium nitrate is used for the washing.

---

[1] It is beyond the scope of this book to go into the details of the procedure. See Hillebrand and Lundell, *Applied Inorganic Analysis*, p. 556.

Common substances interfering in the precipitation of ammonium phosphomolybdate and methods of eliminating or minimizing the interferences are given in Table LVII. Molybdate reagent may take up silica from the glass container in which it is kept. Such a reagent gives an ammonium phosphomolybdate precipitate contaminated with ammonium silicomolybdate. The impure precipitate has a Mo/P ratio greater than 12 and will therefore yield high results in the volumetric method.[1]

Precipitation of magnesium ammonium phosphate in the phosphorus determination.

The errors associated with the precipitation of magnesium as magnesium ammonium phosphate have already been discussed (p. 365). Similar errors are encountered in the precipitation of phosphorus; but it must be remembered that here the conditions are different, the precipitation being made in the reverse way. It is found that if the magnesia reagent is added very slowly to the ammoniacal phosphate solution, the results for phosphorus are low, apparently owing to the formation of a precipitate contaminated with coprecipitated ammonium phosphate. If the reagent is added rapidly, $Mg_3(PO_4)_2$ is coprecipitated; and the results may be high or nearly correct as the result of compensation of errors. If an acid solution of phosphate containing an unregulated excess of magnesia reagent is treated with an excess of ammonium hydroxide, erroneous results are likewise obtained owing to the presence of too much magnesium at the moment of precipitation. Since the amount of phosphorus present is not generally known, it is usually impossible to limit the excess of magnesia mixture to the smallest possible amount. The difficulty can be overcome by dissolving the precipitate in acid and reprecipitating by adding

---

[1] N. Birnbaum and G. H. Walden, Jr., J. Am. Chem. Soc. *60*, 66 (1938).

TABLE LVII. SUBSTANCES INTERFERING IN THE PRECIPITATION OF PHOSPHORUS AS AMMONIUM PHOSPHOMOLYBDATE[1]

SUBSTANCE	EFFECT	PREVENTION OF INTERFERENCE
Sulfuric and hydrochloric acids, and salts of these acids	Retard precipitation and increase solubility of precipitate wnen present in large amounts. Too much nitric acid also increases solubility of precipitate and favors precipitation of MoO_3	Avoid introduction in preparation of sample. Interference not very serious with moderate amounts and can be overcome by adding a larger excess of ammonium molybdate and increasing period of standing. As much as 10 per cent by volume of hydrochloric acid and 5 per cent of sulfuric acid permissible in routine determinations
Hydrofluoric acid and fluorides	Retard precipitation and form a more soluble precipitate	If required in decomposition of sample, volatilize later by evaporation with nitric acid. For small amounts add boric acid to form harmless fluoboric acid
Arsenic	Forms insoluble arsenomolybdate and retards precipitation of phosphomolybdate	May be precipitated with hydrogen sulfide in strong hydrochloric acid solution or volatilized as arsenic trichloride by boiling strong hydrochloric acid solution containing bromide. Small amounts not precipitated if phosphomolybdate is thrown down in the cold
Silicon	Forms insoluble silicomolybdate; may retard precipitation	Remove by dehydrating and filtering off silica at the start
Tungsten	Precipitated	Remove at beginning by digesting with hydrochloric and nitric acids and filtering off tungstic acid; evaporate filtrate with nitric acid to remove chlorides
Titanium, zirconium, and tin	Retard precipitation and may lead to loss of phosphorus through formation of insoluble phosphate	Remove by appropriate means before precipitation of phosphomolybdate. If only small amounts are present, interference can be prevented by addition of small amounts of citrate to ammonium hydroxide used to dissolve yellow precipitate

---

[1] Based mostly upon statements of G. E. F. Lundell and J. I. Hoffman, Ind. Eng. Chem. *15*, 44 (1923).

TABLE LVII. SUBSTANCES INTERFERING IN THE PRECIPITATION OF PHOSPHORUS AS AMMONIUM PHOSPHOMOLYBDATE — *Continued*

SUBSTANCE	EFFECT	PREVENTION OF INTERFERENCE
Vanadium	V^V precipitated as vanadomolybdate. V^{IV} precipitated only in warm solution. Both V^V and V^{IV} retard precipitation of phosphomolybdate	Prevent carrying-down of vanadium by reducing to quadrivalent state and making precipitation at room temperature. Add larger excess of ammonium molybdate and allow to stand longer to overcome retarding of precipitation of phosphomolybdate
Organic substances	May interfere with formation of phosphomolybdate precipitate by forming fairly stable complexes with molybdate (oxalates, tartrates, etc.), thus reducing concentration of active reagent	Destroy by appropriate means, or in some cases add larger excess of molybdate

ammonium hydroxide to the acid solution containing a very little magnesia reagent to reduce the solubility of the magnesium ammonium phosphate. Under these conditions the excess of magnesium ion present at the moment of precipitation is so small that a precipitate having the ideal composition is formed. This procedure, as that for magnesium, furnishes a striking example of the utility of double precipitations in the formation of pure precipitates. It seems vain to attempt to obtain a pure precipitate of magnesium ammonium phosphate by a single precipitation, and the methods of determination of phosphate calling for one precipitation with magnesia reagent are not applicable in accurate work.

The precipitations of magnesium ammonium phosphate are best made in the cold by neutralizing the hydrochloric acid solution slowly with ammonium hydroxide and finally adding a large excess of the latter. The loss of phosphorus on reprecipitation, from solubility of magnesium ammonium phosphate, is negligibly small when the precipitations are made under the proper conditions.

If phosphorus has first been separated as ammonium phosphomolybdate, account must be taken of the possible presence of such elements as titanium and iron in the yellow precipitate. If proper steps to eliminate their interference are not taken, these contaminants will lead to loss of phosphorus when the yellow precipitate is dissolved in ammonium hydroxide, because the phosphates of titanium, iron, and similar elements are insoluble in ammonia and will be left on the filter paper (some is likely to go through the paper and produce a turbid filtrate). By using an ammonium hydroxide solution containing a low concentration of ammonium citrate to dissolve the ammonium phosphomolybdate, this source of error is avoided. Owing to complex formation between citrate, and iron and titanium, the phosphates of these metals dissolve in this solution. Washing the filter paper with dilute hydrochloric acid after passing ammonium hydroxide-ammonium citrate through it assures the complete solution of the phosphorus. The presence of citrate in the solution from which magnesium ammonium phosphate is precipitated prevents the carrying-down of iron, titanium, etc.

Determination of phosphoric anhydride in phosphate rock.

Phosphate rock is an important commercial material used chiefly for the production of phosphatic fertilizers. The value of the rock depends upon its phosphorus content, and the determination of this element is therefore an important one. Phosphate rock is composed primarily of fluoriferous calcium phosphate; the minor constituents include carbonate, chloride, silicates, iron, aluminum, and magnesium. The material is decomposed by a mixture of nitric and hydrochloric acids, or nitric acid alone.

The procedure described below for the determination of phosphorus in phosphate rock involves precipitation of magnesium ammonium phosphate in the presence of much citrate to keep calcium in solution.[1] This procedure is more rapid than the one in which phosphorus is first precipitated as ammonium phosphomolybdate,[2] and gives equally accurate results.

Procedure. Weigh duplicate 0.3–0.35 g. samples of ground material dried at 105° into 250 ml. Erlenmeyer flasks, and treat each as follows. Add 10 ml. of concentrated hydrochloric acid and 2 ml. of concentrated nitric acid, place a small watch glass over the mouth of the flask, and boil gently for one-half hour. Rinse off the cover glass, and add 20 g. of ammonium citrate, 5 ml. of hydrochloric acid, and 60 ml. of magnesia reagent.[3] Neutralize with concentrated ammonium hydroxide, using litmus paper as indicator, and add an excess of 2 ml. Dilute the solution to a volume of 150 ml. with water, add a few glass beads, stopper with a snugly fitting rubber stopper, and shake at intervals for about one-half hour. Then allow to stand overnight.

---

[1] J. I. Hoffman and G. E. F. Lundell, J. Research Natl. Bur. Stand. *19*, 59 (1937).

[2] G. E. F. Lundell and J. I. Hoffman, J. Assoc. Off. Agr. Chem. *8*, 184 (1924).

[3] Prepare as follows: Dissolve 400 g. of magnesium chloride hexahydrate and 300 g. of ammonium chloride in 1500 ml. of warm water. Add ammonium hydroxide until the solution is alkaline to litmus. After one hour filter the solution and add hydrochloric acid to the filtrate until acid to litmus.

Filter through a close-textured paper, and wash the flask and paper once with a small volume of 1 : 20 ammonium hydroxide. Discard the filtrate. Dissolve any precipitate in the flask in approximately 40 ml. of 1 : 4 hydrochloric acid, and pour the solution through the paper. Wash the flask and paper with more of the same acid. Add 0.3 g. of citric acid and 1 ml. of magnesia mixture to the solution, which should have a volume of 75 to 100 ml. While stirring, add ammonium hydroxide until the solution is alkaline to litmus and then an excess of 5 ml. Stir occasionally during one-half hour, and allow to stand for four hours, or overnight.

Collect the precipitate on a 9 cm. close-textured filter paper, and wash with cold 1 : 20 ammonium hydroxide. Transfer the paper to a weighed porcelain or platinum crucible. Char the paper at a low temperature, burn off the carbon below 900°, and ignite to constant weight at 1050°–1100°. Calculate the percentage of P_2O_5.

NOTE. The time of standing in the first precipitation can be reduced to three hours and in the second to two hours if the solution is chilled before shaking or stirring and then allowed to stand in ice water or in a refrigerator at 5° or 10°.

Other weighing forms of phosphorus.

The gravimetric method for phosphorus described above, involving the final weighing of magnesium pyrophosphate, is the most accurate method for ordinary amounts of the element. When small amounts of phosphorus are to be determined, it is permissible to weigh it as ammonium phosphomolybdate after drying the yellow precipitate at 100° to 110°, or as phosphomolybdic anhydride, $P_2O_5 \cdot 24\ MoO_3$, after igniting the precipitate at 400° to 500°:

$$2\,[(NH_4)_3PO_4 \cdot 12\ MoO_3 \cdot 2\ HNO_3 \cdot H_2O] \rightarrow P_2O_5 \cdot 24\ MoO_3 + 4\ HNO_3 + 6\ NH_3 + 5\ H_2O.$$

The advantage of the high molecular weights of these weighing forms is counterbalanced by their more or less uncertain and variable composition. Therefore in accurate determinations phosphorus is never weighed in these forms except when the amount of the element is so small that a slight variation in the composition of the products cannot sensibly affect the result.

When the yellow precipitate is dried at 100° to 110°, it loses the nitric acid originally present and most of the water of crystallization; and the composition of the residue corresponds quite closely to the formula $(NH_4)_3PO_4 \cdot 12\ MoO_3$. The theoretical factor of 1.65 per cent of phosphorus is never strictly applicable; the value of the factor varies to the extent of a few parts per hundred according to the exact method of precipitating, washing, and drying the precipitate. If the precipitate is washed with dilute nitric acid and dried at 110°, the theoretical factor may be used, although the empirical value 1.63 per cent of phosphorus appears to give slightly better results. The precipitate should be collected in a filter crucible. The dried residue is hygroscopic.

The second method mentioned above, in which the precipitate is ignited at 400° or 500° to $P_2O_5 \cdot 24\ MoO_3$, is better than the preceding, because all ammonium salts are expelled and possible errors from variations in composition due to them are eliminated. In this case it is possible to use a solution of ammonium nitrate as a wash liquid, this solution being preferable to dilute nitric acid for this purpose, since the solubility of the precipitate is less in the former. The precipitate is collected in a Gooch or porcelain filter crucible, and the ignition is made in a muffle furnace at 450° or, less preferably, by placing the crucible inside an ordinary crucible and heating with a flame to low redness. The color of phosphomolybdic anhydride is bluish black. If the residue is heated too strongly, its color becomes whitish, and the results are then low owing to volatilization.

It is evident that when either of these weighing forms is used in the determination of phosphorus, care must be taken in the precipitation of ammonium phosphomolybdate to avoid the precipitation of molybdic acid by maintaining the temperature of the solution below 50°. For an application of this method see p. 716.

Other applications of magnesia reagent.

Arsenic in the quinquevalent state can be precipitated quantitatively as magnesium ammonium arsenate hexahydrate by magnesia mixture under conditions very similar to those obtaining in the precipitation of phosphorus. On ignition at high temperatures the precipitate gives magnesium pyroarsenate, and it is weighed in this form. The ignition cannot be made in the presence of organic matter, for then the arsenic is reduced and volatilized. This method is more often applied to the separation of arsenic than to its determination. It is preferable to dissolve the magnesium ammonium arsenate precipitate in strong hydrochloric acid and precipitate the element with hydrogen sulfide as arsenic sulfide and weigh as such.

PROBLEMS

1. If the solubility of $MgNH_4PO_4 \cdot 6\ H_2O$ in water is 0.110 g. per liter at 23°, find the molar concentration of the saturated solution and the number of ml. required to yield 0.100 g. of $(NH_4)_3PO_4 \cdot 12\ MoO_3$.

2. A 0.5204 g. sample of phosphate rock containing 0.71 per cent of moisture yielded an ignition residue of $Mg_2P_2O_7$ weighing 0.3188 g. Calculate the percentage of P_2O_5 in the sample on the wet and the dry basis.

Ans. 39.12 per cent, wet basis; 39.40 per cent, dry basis.

3. A sample of granite weighing 1.15 g. gave 0.0203 g. of $P_2O_5 \cdot 24\ MoO_3$. Calculate the percentage of P_2O_5 and P in the rock.

Ans. 0.068 per cent P_2O_5; 0.030 per cent P.

4. In the determination of P_2O_5 in 85 per cent phosphoric acid (density 1.69), what is the maximum weight of sample that may be taken without having the weight of $Mg_2P_2O_7$ exceed 0.50 g.?

CHAPTER XXV

DETERMINATION OF SILICA

Method.

If the sample is completely decomposable by acids, it is treated with hydrochloric acid; otherwise (and this is the usual case) the silicate must be fused with sodium carbonate, and the melt, which contains the silicate in acid-decomposable form, is then treated with hydrochloric acid. In either case the acid solution of the decomposed sample is evaporated to dryness to separate the silica as insoluble $SiO_2 \cdot x\, H_2O$, and the residue is heated at 100° to 120° partially to dehydrate the silica and to render it as insoluble as possible. The residue is extracted with hot dilute hydrochloric acid to dissolve salts of iron, aluminum, the alkali metals, etc., which may be present. The greater portion of the silica remains undissolved and is filtered off. The filtrate is evaporated to dryness, and the residue is baked as before to dehydrate and render insoluble the small amount of silica that has escaped separation. The residue is treated with dilute hydrochloric acid as before, and the second portion of silica is filtered off on a fresh filter. The two washed precipitates, containing practically all of the silica originally present in the sample, are ignited in a platinum crucible to silicon dioxide, and the latter is weighed. The ignited residue is usually not entirely pure but will contain small amounts of the oxides of titanium, aluminum, iron, etc. To obtain the weight of silicon dioxide present, the impure silica is treated with hydrofluoric and sulfuric acids, which treatment results in the volatilization of the silica as silicon tetrafluoride. The residue is strongly heated to convert the sulfates of aluminum, iron, etc. into the corresponding oxides, in which form these metals were originally present; and the crucible is then weighed. The loss in weight represents the amount of silica.

Decomposition of silicates.

The solubility of a silicate in strong acids depends largely upon the proportion of silica in the silicate, and upon the solubility of the metal oxide or oxides present, which in turn is a function of the basicity of the metal. Other things being equal, the greater the ratio of silica to bases in a silicate, the less easily will the silicate be attacked by acids. The more basic the metals present, the more easily will the silicate be decomposed by acids. Thus, the sodium silicates are freely soluble in water, calcium silicate ($CaSiO_3$) is insoluble in water but readily decomposed by dilute acids, while a silicate such as Al_2SiO_5 is hardly acted upon by acids. A silicate containing much essential water is likely to be acid-decomposable. Among important silicates encountered, the following can be decomposed by heating with mineral acids: Portland cement, blast-furnace slag, and the zeolites.

The great majority of the silicates found in nature, as well as many artificial ones (glass, porcelain), cannot be completely decomposed by acid treatment. These, however, can all be brought into a form completely decomposable by acids by fusion, or strong heating, with an alkali. This treatment results in an increase in the proportion of bases in the silicate, thereby rendering it acid-decomposable. The alkali commonly used for this purpose is sodium carbonate.[1] A part of the sodium combines with the silica, and an equivalent amount of carbon dioxide is liberated. The fusion is always made with a large excess of sodium carbonate to insure complete acid-decomposability of the product. The silicate must be ground exceedingly fine, and a high temperature must be employed in the fusion, or else decomposition is likely to be incomplete. The fusion is made in platinum, this metal not being attacked to any significant extent by molten sodium carbonate.

Although sodium carbonate is commonly the reagent used for the decomposition of refractory silicates, there are some other alkaline substances that find considerable application. One of these is sodium hydroxide. It acts much more vigorously upon silicates than does sodium carbonate; it can be obtained in a rather high degree of purity, but less easily so than sodium carbonate, and moreover is less easily kept in a pure state than the latter. Molten sodium hydroxide attacks platinum, and such crucibles cannot be used for the fusion. Nickel crucibles are suitable, although the melt is contaminated by nickel to a greater or lesser extent depending upon the fusion temperature; if the temperature is not allowed to rise above 500° (and this is sufficiently high for rapid decomposition), the amount of nickel dissolved is very small, provided bright crucibles of the metal are used (p. 181). The sodium hydroxide must first be fused alone in the crucible to expel the water which it contains and which would otherwise cause spattering with losses; the sample is then added. Decomposition of silicates, and other materials as well, with sodium hydroxide finds valuable applications, especially in the analysis of technical materials in which only one or a few constituents are to be determined.[1] This flux is less often used when a complete analysis of a silicate is to be made (e.g., rock analysis).

---

[1] Sodium carbonate is used in preference to the potassium salt, especially because the latter is deliquescent. Formerly a mixture of the two carbonates was employed, it having a lower melting point than either component. In these days when it is easy to melt sodium carbonate with the burners found in every laboratory, it alone should be used because the decomposition is aided by the high temperature of the melt.

Sodium peroxide is a powerful disintegrator, sometimes employed in the analysis of siliceous materials when an oxidizing flux is required.[2] It is used in iron or nickel crucibles.

For the determination of the alkalies in silicates by the J. Lawrence Smith method, the flux employed is a mixture of calcium carbonate and ammonium chloride, which on heating yields calcium oxide and calcium chloride. It is the basic mixture of the latter two substances which is the active reagent (see p. 751).

When silica is not to be determined, the silicate may be decomposed by heating with hydrofluoric and sulfuric acids (for an example, see p. 756). Silicon is volatilized as silicon tetrafluoride, and the metals are left as sulfates. A few silicates are not easily decomposed by hydrofluoric acid.

Analytically important properties of silicic acid (hydrated silica). Silicic acid is one of the weakest of inorganic acids, its ionization constant being of the order of 10^{-10}. The soluble silicates are largely hydrolyzed in aqueous solution; the silicic acid exists in the colloidal form in such solutions. When a strong acid is added to a silicate solution, the silicic acid is coagulated; and usually more or less of the gelatinous hydrogel separates. It is not possible to coagulate and precipitate all of the silicic acid by simply adding a strong acid to the silicate solution and boiling. When formed by acidification of a silicate solution, silicic acid is the most hydrophylic of the inorganic colloids, and a special treatment is required to separate hydrated silica from its colloidal solutions with any degree of completeness; viz., it is necessary to evaporate the acid solution to dryness if hydrochloric acid is present, or to fumes if sulfuric or perchloric acid is in solution, and to heat for some time at 100° or slightly higher. During the heating the hydrated silica loses considerable amounts of water and is rendered "insoluble," by which is meant that the dried substance displays only a small tendency to go into colloidal solution again with dilute acids. The true, or molecular, solubility of dehydrated silica is extremely small. After drying at 100°, the residue has the approximate composition $SiO_2 \cdot \frac{1}{2} H_2O$ but is not to be regarded as consisting of any definite hydrate.

---

[1] See, for example, C. J. van Nieuwenburg and H. H. Dingemans, Chem. Weekbl. *25*, 266 (1928), and especially O. Brunck and R. Holtje, Angew. Chem. *45*, 331 (1932).

[2] W. F. Muehlberg, Ind. Eng. Chem. *17*, 690 (1925).

The colloidal behavior of silica is very complex. Freshly formed silicic acid, obtained by adding acid to a silicate solution under the proper conditions, appears to form a true molecular solution. First monosilicic acid, $Si(OH)_4$, is formed, which on standing is transformed more or less rapidly into polyacids, the speed of the reaction being greatly dependent upon the pH of the solution (maximum stability at pH 2 to 3).[1] Finally aggregates of high molecular weight are formed which are insoluble in water but which can form colloidal solutions. The behavior of colloidal silica solutions is very complicated. The reason probably is that they have properties intermediate between hydrophobic and hydrophylic sols (see p. 94). The stability of the former is mainly determined by the electrical charge, and complete flocculation is obtained upon addition of suitable amounts of electrolytes. In addition to the charge, the stability of hydrophylic colloids is determined by the degree of hydration. By removal of the electric charge and the adsorbed water layers, the silica is rendered insoluble in water. In analytical work this is accomplished by evaporation of the solution of the silica to dryness in the presence of acid, heating the residue at about 100°, and taking it up in dilute hydrochloric acid.

When the baked residue of the partially dehydrated silica is taken up in dilute acid to extract the soluble salts, a small amount of silica reverts to the colloidal condition and goes into solution;[2] but the greater part remains undissolved and can be filtered off and washed free from soluble salts. The combined filtrate and washings must be evaporated to dryness and the residue again heated at 100° + to render the remainder of the silica "insoluble." The second portion of the silica must be collected in a new filter paper. If it were collected in the first filter, some of the original silica would go back into the solution as the result of colloidal dispersal. The filtrate from the second dehydration will contain very small amounts of silica, but further evaporations and dehydrations do not result in the recovery of any significant amounts of the substance.[1]

---

[1] F. Mylius and E. Groschuff, Ber. *39*, 116 (1906); R. Willstätter, H. Kraut, and K. Lobinger, Ber. *61*, 2280 (1928); *62*, 2027 (1929).

[2] For experiments on the "solubility" of hydrated and anhydrous silica, see V. Lenher and H. V. Merrill, J. Am. Chem. Soc. *39*, 2630 (1917).

Silica hydrogel possesses rather strong adsorptive powers and, being negatively charged, shows a distinct tendency to carry down such metals as aluminum and iron. The salts of these and other metals are held strongly by the silica and cannot be entirely removed by extracting and washing the residue with dilute hydrochloric acid.

Dehydration of the silica.

The acid most commonly used for the decomposition of an acid-decomposable silicate or for the solution of the sodium carbonate melt of a refractory silicate is hydrochloric acid. As already stated, it is necessary to evaporate the decomposed silicate to dryness with excess acid and to heat for some time at 100° to 120° to render the hydrated silica as "insoluble" as possible. This operation must be carried out in a porcelain casserole or a platinum dish;[2] a glass beaker, even if of the resistant variety, must not be used.

In the first dehydration it suffices to evaporate to complete dryness without further heating, although it may be advantageous to heat the residue at 100° to 110° for one hour. The dehydration should not be prolonged over an hour, nor should the temperature be much over 110°, else it is likely that the amount of foreign substances contaminating the silica will be increased; moreover, there is then the possibility if magnesium is present that some of the silica will be rendered pseudo-soluble as the result of interaction with the basic magnesium chloride formed in the dehydration. The residue is taken up in dilute hydrochloric acid, never in water. The dilute acid serves to extract the slightly soluble basic salts of iron, aluminum, magnesium, etc. produced in the heating and reduces the amount of silica going into colloidal solution. It appears that the amount of silica reverting to the colloidal condition increases with the acid concentration above a certain value. A 10 per cent solution of hydrochloric acid gives better results than a stronger solution.[1] In the presence of hydrolyzable salts such as those of titanium, iron, and aluminum, it is found to be advantageous to moisten the residue with concentrated hydrochloric acid and then to dilute the acid after a short period of contact. The dilute acid solution is heated to boiling to aid the leaching-out of the soluble constituents of the residue. This heating should not be unnecessarily prolonged, because the amount of colloidal silica tends to increase with the time of heating. The first portion of the silica is best washed with *hot* dilute hydrochloric acid. The use of water as the wash liquid is inadmissible. There would then be a great likelihood of the formation of slightly soluble basic salts of titanium, iron, and aluminum as the result of hydrolysis.

---

[1] For investigations on the dehydration of silica from the analytical standpoint, see W. F. Hillebrand, J. Am. Chem. Soc. *24*, 362 (1902); V. Lenher and E. Truog, J. Am. Chem. Soc. *38*, 1050 (1916).

[2] A platinum vessel is to be preferred to one of porcelain, but in instructional laboratories the extensive use of platinum is usually out of the question. A little silica is likely to be introduced from a porcelain dish during the evaporation, but this gain may be more than counterbalanced by a small loss resulting from the difficulty of removing all the silica from the dish (silica adheres tenaciously to porcelain).

The amount of silica recovered in the first dehydration usually amounts to 97 to 99 per cent of the total present. The second evaporation and dehydration recover the greater percentage of the remainder. In the second dehydration it is admissible to keep the residue at 110° for one hour. For washing, a cold 1 : 100 solution of hydrochloric acid should be used.[2] A third evaporation and dehydration are not carried out, for if the previous dehydrations have been carefully made, very little, if any more, silica will be obtained. Notwithstanding that no more silica can be recovered by evaporation, there still remains a small quantity in the filtrate from the second evaporation.[3] No account is taken in the procedure below of the silica that thus escapes separation. The error thus knowingly made is relatively small but must be taken into account in very accurate analysis. The small amount that remains will be carried down, although not completely, in the ammonia precipitate in the course of a complete analysis and can be recovered from the latter (see the procedure given on p. 738). The silica remaining in solution after two evaporations may be more than compensated for by the introduction of silica from the reagents and vessels if a blank is not run.

---

[1] Thus H. T. Bucherer and F. W. Meier, Z. anal. Chem. *82*, 41 (1930), found that working under otherwise constant conditions 3.2 mg. of silica went into solution with 10 per cent acid, 5.4 mg. with 15 per cent, and 9.2 mg. with 20 per cent acid.

[2] Recommendation of Hillebrand and Lundell, *Applied Inorganic Analysis*, p. 543.

[3] See the table in Hillebrand and Lundell, *Applied Inorganic Analysis*, p. 541, for the amounts of silica left in solution after double evaporations in the analysis of various materials.

Use of acids other than hydrochloric in the dehydration of silica. Instead of hydrochloric acid it is possible to use sulfuric or perchloric acid in the dehydration of silica. In the concentrated form (constant-boiling mixture) both of these acids possess powerful dehydrating properties. By evaporating a soluble silicate with either acid to the point of fuming, the greater proportion of silica present is rendered insoluble. Sulfuric acid is not very frequently used because it gives anhydrous sulfates with a number of metals which are only difficultly soluble in the diluted acid mixture (the acid must be diluted before filtration) and, moreover, barium, lead, and calcium sulfates are insoluble or very slightly soluble and would therefore contaminate the silica. Perchloric acid does not possess these disadvantages and has been recommended for the dehydration of silica by Willard and Cake.[1] With the exception of potassium, all of the metal perchlorates are freely soluble in water or dilute perchloric acid solutions. In the presence of metals yielding insoluble chlorides, perchloric acid is substituted for hydrochloric acid in the analysis of silicates; and in other cases its use may be advantageous. The dehydration is accomplished in less time with perchloric than with hydrochloric acid, and the precipitated silica is often purer in the former case. However, one evaporation to fumes with perchloric acid does not result in the recovery of all the silica, very appreciable amounts remaining in solution.[2]

Van Tongeren [3] compared various methods for the determination of silica in acid-soluble silicates (Portland cement) and found that the best results were obtained by mixing the sample with ammonium nitrate, heating with concentrated nitric acid, filtering off the separated silica, and washing with 5 per cent nitric acid containing a few drops of hydrogen peroxide. The silica separated in this manner is said to be purer than that obtained by evaporating with hydrochloric or perchloric acid, and moreover the separation is so complete that in most cases the filtrate need not be evaporated to recover remaining silica.

Obtaining the true weight of silica in the ignition residue.

The washed precipitates of silica are heated to a high temperature [4] (Meker burner or blast lamp) in a platinum crucible to obtain anhydrous silica (SiO_2). Care must be taken in this operation to prevent mechanical loss of the light, fluffy residue. The ignited silica is hygroscopic and must therefore be cooled and weighed with due precautions.

As already mentioned, the weight of the ignited residue does not represent the weight of silica present, because silica separated as described above is always contaminated with greater or less amounts of nonvolatile contaminants. Small amounts of basic salts of titanium, aluminum, and iron are tenaciously retained by the hydrous silica and cannot be entirely removed by washing with dilute hydrochloric acid.[1] Furthermore, substances insoluble *per se* may be present in the separated silica. Thus, it is common to find both titanium and phosphorus in silicates. These form titanium phosphate, which is only slightly soluble in dilute acids and is therefore left to a large extent with the dehydrated silica. If large amounts of calcium and sulfur should be simultaneously present (natural waters), insufficient washing of the silica precipitate may leave calcium sulfate associated with it.

---

[1] H. H. Willard and W. E. Cake, J. Am. Chem. Soc. *42*, 2208 (1920).

[2] A procedure for the determination of silica in acid-soluble silicates involving the use of a mixture of perchloric and hydrochloric acids has been given by F. W. Meier and O. Fleischmann, Z. anal. Chem. *88*, 88 (1932).

[3] W. van Tongeren, Chem. Weekbl. *34*, 774 (1937).

[4] W. Miehr, P. Koch, and J. Kratzert, Z. angew. Chem. *43*, 250 (1930), state that after heating to the indicated temperatures for one hour and cooling for one-half hour in a desiccator, the ignited silica contains the following percentages of water: 900°, 0.9; 1000°, 0.5; 1100°, 0.2; 1200°, 0.1.

Fortunately silicon forms a gaseous fluoride, and the silica in the impure ignited residue may therefore be obtained from the loss in weight resulting from the treatment of the residue with hydrofluoric acid, provided that the contaminants are in the same form, i.e., possess the same weight, before and after the hydrofluoric acid treatment and are not volatilized in the operation. The fulfillment of these requirements is assured by conducting the hydrofluorization in the presence of sulfuric acid [2] as explained in the next paragraph. The reaction taking place between silica and hydrofluoric acid is represented by the following equations:

$$SiO_2 + 6\,HF \rightleftarrows H_2SiF_6 + 2\,H_2O$$
$$H_2SiF_6 \rightleftarrows SiF_4 + 2\,HF.$$

The last reaction proceeds to the right on heating. It may be noted that the presence of sulfuric acid displaces the equilibrium in the first reaction to the right on evaporation, owing to the dehydrating properties of this acid.

After the silica precipitate has been strongly ignited, the principal contaminants will be present as the oxides (TiO_2, Al_2O_3, Fe_2O_3). Now, if sulfuric acid were omitted in the evaporation of the silica with hydrofluoric acid in the expulsion of silicon as the tetrafluoride, the contaminating metals would be left as the fluorides after the ignition of the residue; with the exception of titanium, which would be lost, its fluoride, TiF_4, being volatile.

---

[1] The alkali and alkaline earth metals are usually not found in significant amounts in the silica precipitate, chiefly because the salts of these metals do not hydrolyze to form slightly soluble basic salts. K. Rankama, Compt. rend. soc. géol. Finlande No. 14 (1939), has studied the composition of the residue from silica obtained in rock analysis.

[2] For the use of perchloric-oxalic acid instead of sulfuric acid, see J. Billheimer, P. H. Faust, and E. H. Swift, Ind. Eng. Chem., Anal. Ed. *12*, 409 (1940).

Consequently, erroneous results would be obtained in calculating the amount of silica present from the loss in weight. The difficulty is avoided by adding sulfuric acid with the hydrofluoric acid. After the evaporation of the latter the contaminating metals are left as sulfates (titanium is not volatilized). During the subsequent ignition the sulfates of titanium, aluminum, and iron are decomposed into the oxides, e.g.:

$$Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3\ SO_3.$$

The decomposition of the sulfates of these metals is complete far below 1000°. The final ignition should be conducted over a Meker burner or blast lamp but need not be continued long because of the small amount of residue present.[1]

Determination of silica in an acid-insoluble silicate.

Procedure. Reduce 2 or 3 g. of coarsely powdered sample to a very fine powder in an agate mortar, grinding only small portions at a time. Weigh out duplicate samples of 0.8 g. into platinum crucibles of 20 to 30 ml. capacity. Next, weigh out on a watch glass 4 (± 0.2) g. of purest anhydrous sodium carbonate. Place the crucible on a sheet of paper, and by means of a spatula transfer approximately three fourths of the sodium carbonate to the crucible. Intimately mix the silicate powder and the flux by stirring gently with a platinum spatula or a short glass rod with rounded ends; be careful not to scratch the crucible or to raise dust. The mixture should finally appear homogeneous; care should be taken to see that no unmixed sample remains at the bottom of the crucible. Tap the spatula or glass rod to cause any adhering particles

[1] A few words may be said here of the effect of other contaminants, less usually present in appreciable amounts, upon the indirect determination of silica by hydrofluorization. The sulfates of magnesium and manganese are decomposed completely into the oxides at temperatures slightly below 1000°. In the case of manganese the oxide is of somewhat variable composition. Calcium sulfate when pure gives the oxide when heated to approximately 1200°, but at lower temperatures in the presence of silica. The presence of this sulfate in the impure silica gives rise to some uncertainty in the determination of silica by difference.

The presence of alkali chlorides is very objectionable. These should not be present in the silica; but if the precipitate has not been carefully washed (especially after a sodium carbonate fusion of the sample), they may be found in it. The alkali remaining unvolatilized will be weighed as the chloride before the hydrofluoric acid treatment and as the sulfate after. The result for silica will then be low. The error can be reduced by moistening the precipitate with sulfuric acid before the first ignition but not entirely eliminated because an alkali silicate may be formed during the ignition (Hillebrand and Lundell, *Applied Inorganic Analysis*, p. 545). When phosphate contaminates the silica, it is necessary to fume off the sulfuric acid at as low a temperature as possible to minimize the volatilization of phosphoric acid.

to fall into the crucible, and rub the spatula on the sodium carbonate on the watch glass to remove any powder possibly sticking to it. Transfer all the remaining sodium carbonate to the crucible, covering the mixture with a uniform layer of flux.

Place the covered crucible vertically upon a clay triangle, and begin the heating with a very low Tirrill flame; it is safest to support the crucible first about 10 cm. above the flame. After 5 to 10 minutes lower the crucible and gradually increase the height of the flame until the bottom of the crucible is faint red. After another 10 minutes raise the temperature slowly until the mass is in quiet fusion (lift the cover slightly with the crucible tongs). Keep the contents at this temperature for about 30 minutes; there should be but little bubbling of the molten mass during this period; the crucible must be kept covered. Finally apply the full heat of the Tirrill burner (or Meker if necessary) for 10 to 15 minutes. Remove the burner, lay aside the cover of the crucible, grasp the crucible with the tongs, and give it a slow rotary motion so that the molten contents will spread over the sides and solidify as a thin shell over the interior. This procedure will later facilitate the removal of the contents. Set the crucible on a clean stone surface to cool, or return it to the triangle, replacing the cover.

When the crucible is thoroughly cold, and not before, fill it approximately one-third full with water. After a few minutes heat the crucible cautiously with a low flame; do not boil the liquid. Touch the cake with a 6 to 7 cm. glass rod to see if it has been loosened. If it has not, pour the liquid into a 300 ml. porcelain[1] casserole, being careful to wash off the drop that remains adhering to the outside of the crucible. Again add water to the crucible, and heat. If, after repeating this procedure once or twice, the cake does not loosen, rinse off the outside of the crucible, place it on its side in the casserole, and fill the latter about one-third full with water. Warm, and stir until the cake disintegrates and can be easily removed. By means of a 15 cm. stirring rod lift the crucible out of the liquid; and, while holding it a few cm. above the liquid, wash its interior and exterior thoroughly with water. Hold the crucible cover over the crucible, pour a few drops of dilute hydrochloric acid upon the under side of the former to dissolve any sodium carbonate that may have spattered on to it during the fusion, and rinse the crucible, finally adding the solution to the casserole. Pour very slowly 20 ml. of concentrated hydrochloric acid into the *covered* casserole.[1] The solution of the cake may be aided by disintegrating it with a rod. When the evolution of carbon dioxide has ceased, rinse off the cover glass and the sides of the dish above the liquid. Some gelatinous silicic acid will usually be visible at this point. There should be no gritty particles present; if such are found, the decomposition is most likely incomplete, and a new sample must be fused with sodium carbonate, greater care being taken this time to insure complete decomposition.

---

[1] A platinum dish is better.

Place the dish on the steam bath, and evaporate the contents to dryness. Heat the residue for one hour on the steam bath, and then add 5 ml. of concentrated hydrochloric acid. With the aid of a stirring rod bring the acid in contact with all the solid in the dish. Add 75 ml. of water, rinse down the sides of the dish, and leave the stirring rod in the vessel. Heat the casserole on the steam bath or over a low flame, stirring the contents to aid solution of the soluble salts, until only silica remains undissolved. Filter through a 9 cm. filter paper of medium texture, and receive the filtrate in a 250 ml. beaker. Transfer as much as possible of the silica to the paper, rinse the casserole with a warm solution of 1 : 20 hydrochloric acid, and wash the precipitate thoroughly with the same wash liquid and finally once with water. Pour the filtrate which has been collected in the beaker into the original casserole, rinse out the beaker, and evaporate the solution to dryness. Heat the residue at 100° to 105° for one-half hour. Moisten the separated salts with 1 to 2 ml. of concentrated hydrochloric acid, add 25 ml. of water, heat to extract soluble salts, and filter through a fresh filter paper. Rinse out the dish, and carefully wash the precipitate with cold 1 : 100 hydrochloric acid. To remove any silica adhering to the casserole, rub the interior of the latter with one or two small pieces of moist quantitative filter paper, using the stirring rod for this purpose. Place this paper in the filter. Discard the filtrate (except when other constituents are to be determined in the solution).

Fold up the moist filters, and place them in a platinum crucible. Dry the filter papers by heating the covered crucible, placed in the vertical position, with a very low Tirrill flame. When all water has been expelled, lower the crucible and char the paper. When the volatile matter has been driven off, slide the cover slightly to one side, and increase the flame to burn off the carbon, still keeping the crucible vertical. Then, when all the carbon has been burned off, cover the crucible tightly, replace the Tirrill burner with a Meker, and apply the full heat of the latter for one-half hour. Cool the crucible in a desiccator, weigh, and reheat to constant weight, using fifteen-minute periods of heating. Remember that ignited silica is hygroscopic.

---

[1] It is best to add the acid through a small funnel inserted beneath the cover glass (p. 246).

Moisten the residue with 1 to 2 ml. of water, adding the latter from a pipet inserted below the cover. Add 4 or 5 drops of 1 : 2 sulfuric acid and then, carefully, about 5 ml. of hydrofluoric acid. Place the crucible in a radiator (less preferably on a hot plate), and evaporate off the hydrofluoric acid in a hood without boiling the liquid. When only sulfuric acid remains, increase the heat and fume it off. Then heat the crucible strongly for ten to fifteen minutes with the direct full flame of a Tirrill burner. Cool and weigh the crucible. From the loss in weight calculate the percentage of SiO_2 in the sample.

Regarding the running of a blank, see p. 287. It is important that the hydrofluoric and sulfuric acids used be free from nonvolatile impurities. It is safest to test them by evaporating the same volumes as used in the procedure in a platinum crucible and obtaining the weight of the ignited residue.

PROBLEMS

1. What is the minimum volume of hydrofluoric acid (sp. gr. 1.15, 46 per cent HF) and of sulfuric acid (sp. gr. 1.84, 96 per cent) required to decompose 1.00 g. of a silicate of the following percentage composition and convert the metals into the normal sulfates?

SiO_2	60	MgO	4
Al_2O_3	15	CaO	5
Fe_2O_3	4	Na_2O	4
FeO	5	K_2O	3

2. From the following analytical data obtain the formula of a hydrated magnesium silicate:

(a) A 1.120 g. sample yielded 0.1445 g. of essential water.

(b) A 0.3621 g. sample gave 0.4362 g. $Mg_2P_2O_7$.

(c) On treatment with hydrofluoric and sulfuric acids the ignited silica residue from a 0.9870 g. sample showed a loss of 0.4278 g.

3. An ignited silica residue weighing 0.5050 g. and containing 1.0 per cent of sodium chloride is treated with hydrofluoric and sulfuric acids and silica determined by loss in the usual way. How great is the resulting error?

Ans. − 2.2 parts per thousand.

CHAPTER XXVI

DETERMINATION OF SODIUM AND POTASSIUM

The determination of the alkali metals is one of the less easy problems of analysis. Owing to the comparatively great solubility in water of even the less soluble salts of these metals, special precipitation procedures involving, for example, the use of organic solvents must be applied. In the usual case (natural samples) the determination of both potassium and sodium is required. Two methods are available when both alkalies are to be determined: (1) potassium and sodium may both be determined directly, or (2) either potassium or sodium can be determined, and the other alkali then found by difference from the sum of the two, for example, as the chlorides. The rarer alkalies, lithium, rubidium, and cesium, are encountered so rarely or occur in such small quantities with sodium and potassium that they will not be considered here.[1]

When either sodium or potassium is present alone as a salt of an organic acid or a volatile inorganic acid (chloride, bromide, iodide, nitrate, carbonate, etc.), it may be determined by conversion to the sulfate and weighing the latter. The alkali sulfates are preferred to the chlorides as weighing forms because the latter volatilize at much lower temperatures. In brief the determination is made as follows. The sample (evaporated if necessary) is treated with dilute sulfuric acid, and the excess acid is removed by fuming. There is thus obtained an alkali sulfate containing greater or lesser amounts of pyrosulfate. The sulfur trioxide cannot easily be quantitatively expelled from the pyrosulfate by ignition, so there are added successive small portions of ammonium carbonate, which react with the pyrosulfate to give the normal sulfate and ammonium sulfate, the latter being volatilized. The sulfate is then ignited to constant weight. Sodium sulfate can be rendered entirely water-free by heating to 900° (slightly above the melting point) without loss by volatilization. Heated at 400° to 700°, the salt contains only about 0.05 per cent of water. Potassium sulfate can be heated in the range of 400° to 800° but not above the latter temperature on account of loss by volatilization.[2]

Direct determination of potassium.

There are two common methods for the determination of potassium in the presence of sodium. One involves the precipitation of potassium as the chloroplatinate and the weighing of this compound or of the platinum formed from it by reduction; and the other is the precipitation as potassium perchlorate, which is weighed as such. These are practically the only forms in which the element can be separated and accurately determined in the presence of sodium.[1]

---

[1] For the determination of lithium see, for example, S. Palkin, J. Am. Chem. Soc. *38*, 2326 (1916) and E. R. Caley and H. D. Axilrod, Ind. Eng. Chem., Anal. Ed. *14*, 242 (1942); see also the note on p. 415 in this chapter. Regarding the separation of potassium, rubidium, and cesium, refer to R. C. Wells and R. E. Stevens, Ind. Eng. Chem., Anal. Ed. *6*, 439 (1934); *9*, 236 (1937).

[2] H. Remy and R. Siegmund, Z. anal. Chem. *93*, 321 (1933).

The chloroplatinate method is generally considered the more accurate of the two, although it suffers from the disadvantage of requiring an expensive reagent;[2] moreover, the precipitate of potassium chloroplatinate usually does not have quite the composition corresponding to the formula K_2PtCl_6, and an empirical factor is therefore generally applied in calculating the weight of potassium from the weight of the precipitate. The perchlorate method is the more recent of the two methods. It is now used extensively and gives very satisfactory results.

1. *The chloroplatinate method.* This method is based on the insolubility of potassium chloroplatinate in 80 per cent ethyl alcohol and the free solubility of sodium chloroplatinate in the same liquid.[3] The reagent used is chloroplatinic acid. The sample in the form of the chlorides of the alkali metals,[4] and free from other substances, is treated with an excess of chloroplatinic acid; and the solution is evaporated to a small volume. The chlorides of the two metals are thus converted into the corresponding chloroplatinates with the simultaneous expulsion of hydrochloric acid:

$$2\,KCl + H_2PtCl_6 \rightarrow K_2PtCl_6 + 2\,HCl$$
$$2\,NaCl + H_2PtCl_6 \rightarrow Na_2PtCl_6 + 2\,HCl.$$

It is very important to add enough reagent to convert sodium into the chloroplatinate, because sodium chloride is insoluble in 80 per cent alcohol. The residue of the chloroplatinates and excess chloroplatinic acid is then extracted with 80 per cent alcohol. Sodium chloroplatinate and the excess of reagent dissolve in the alcoholic solution, whereas the potassium salt remains undissolved and is weighed after washing and drying at 135°. As already mentioned, the dried residue does not have the exact composition

---

[1] Innumerable procedures have been proposed for the determination of potassium as the cobaltinitrite by precipitation with sodium cobaltinitrite, but none appears to give highly accurate results. For certain purposes the results obtained by the method are sufficiently good to warrant its use. The precipitate formed when sodium cobaltinitrite is added to a solution of a potassium salt always contains sodium, is usually ascribed the formula $K_2NaCo(NO_2)_6$, and under certain conditions of precipitation approximates this composition closely. The ratio of sodium to potassium in the precipitate is variable and depends upon the ratio of the two metals in the solution as well as upon the conditions of precipitation. L. V. Wilcox, Ind. Eng. Chem., Anal. Ed. *9*, 136 (1937), claims that good results can be obtained by using pure trisodium cobaltinitrite as reagent and precipitating in nitric instead of acetic acid solution.

[2] However, the platinum in the precipitate and the filtrate can be recovered and reconverted into chloroplatinic acid and used over and over again. See M. C. Swisher and F. F. Hummel, Ind. Eng. Chem., Anal. Ed. *11*, 162 (1939), regarding the recovery of platinum.

[3] Potassium and sodium chloroplatinates do not form mixed crystals nor double salts. Potassium chloroplatinate crystallizes in the isometric system and the sodium salt, $Na_2PtCl_6 \cdot 6\,H_2O$, in the triclinic system.

[4] Obtained, for example, as described on pp. 748 *et seq.*

K_2PtCl_6,[1] and it is customary to use the empirical factor 0.3056 [2] in place of the theoretical value $\frac{2\ KCl}{K_2PtCl_6} = 0.3067$ in calculating the weight of potassium chloride from the weight of potassium chloroplatinate dried at 130° to 140°. In the most careful work the value of the factor for the particular reagent used and procedure followed should be obtained by finding the weight of potassium chloroplatinate yielded by a known amount of pure potassium chloride.

Alcoholic solutions stronger than 80 per cent by volume are avoided in the extraction of the mixed chloroplatinates as possibly leading to the decomposition of sodium chloroplatinate:

$$Na_2PtCl_6 \rightarrow 2\ NaCl + PtCl_4.$$

The solubility of potassium chloroplatinate in 80 per cent alcohol at 20° is approximately 4 mg. per 100 ml. The solubility loss of potassium in the procedure is negligibly small if care is taken to restrict the alcohol solution to the minimum volume required; it is to be borne in mind that the presence of an excess of the reagent as well as of the sodium chloroplatinate and the non-attainment of solubility equilibrium in washing lead to a much smaller loss by solubility than would be indicated by the figure given.

Ammonium, rubidium, and cesium all yield chloroplatinates insoluble in alcohol and are counted with potassium if present. Ammonium salts can be removed very easily by ignition of the mixed chlorides at a low temperature. Lithium chloroplatinate is soluble in alcohol and therefore accompanies sodium into the filtrate. Sulfate must not be present because sodium sulfate is insoluble in the alcoholic solution. In general, substances other than the alkali chlorides should be absent; however, small amounts of calcium, magnesium, and strontium chlorides are usually permissible.

It is often advantageous in practical analysis to reduce the platinum in the washed potassium chloroplatinate precipitate to the metal and

---

[1] The reasons for this have variously been ascribed to the presence of such compounds as $H(NO)PtCl_6$ or $H_2PtOHCl_5$ in the chloroplatinic acid, to the hydrolysis of the precipitate by the water in the alcohol:

$$K_2PtCl_6 + H_2O \rightarrow K_2Pt(OH)Cl_5 + HCl,$$

and to the partial reduction of the precipitate by the aldehyde which is always present in small amounts in ordinary alcohol:

$$K_2PtCl_6 + CH_3CHO + H_2O \rightarrow K_2PtCl_4 + CH_3COOH + 2\ HCl$$
$$K_2PtCl_4 \rightarrow 2\ KCl + PtCl_2.$$

The last-mentioned explanation is offered by R. Strebinger and H. Holzer, Z. anal. Chem. *90*, 81 (1932). Moreover the residue dried at 135° is not entirely free from water.

G. F. Smith and A. C. Shead, J. Am. Chem. Soc. *53*, 947 (1931), have shown that when purified lithium chloroplatinate is used instead of chloroplatinic acid the precipitated potassium chloroplatinate has the theoretical composition and the theoretical factor can be used in the computation. Moreover the potassium chloroplatinate obtained with lithium chloroplatinate as reagent can be dried at 260°, whereas the impure salt decomposes above 160°.

[2] R. Fresenius, Z. anal. Chem. *21*, 234 (1882). Careful work by H. Fresenius and P. H. M. Brinton, Z. anal. Chem. *50*, 21 (1911), shows that highly accurate results are obtained when this factor is applied.

obtain the weight of the potassium present from the ratio 2 K : Pt. When the platinum in the precipitate, and not the precipitate itself, is weighed, it is possible to determine potassium in the presence of sulfates, phosphates, calcium, magnesium, and indeed most other metals.[1]

Procedure. The following directions apply to the determination of potassium in a mixture of potassium and sodium (lithium) chlorides containing no other substances.

Dissolve a weighed sample of suitable size (generally not over 0.25 g.) in 5 to 10 ml. of hot water in a small porcelain dish. Add enough pure chloroplatinic acid solution containing 0.1 g. of platinum per milliliter to combine with all the alkali present, assuming for safety that the sample is composed entirely of sodium chloride. No precipitate should form at this point. Place the dish on the steam bath and evaporate nearly, but not quite, to dryness; the syrupy liquid should solidify on cooling. Add 10 ml. of 80 per cent (by volume) ethyl alcohol[2] to the cold dish, and break up the residue with a short stirring rod having a flattened end. After thorough disintegration, decant the supernatant solution through a small paper filter, leaving as much as possible of the precipitate in the dish. Continue to extract the residue in the dish, using successive small portions (1–2 ml.) of 80 per cent alcohol, decanting through the filter each time until the alcohol runs through entirely colorless. The salt then remaining in the dish should be golden-yellow in color; an orange-red coloration indicates the presence of sodium chloroplatinate. These operations should all be conducted in a place free from ammonia fumes. When all the sodium has been extracted, dry the filter and the dish to remove the alcohol. Then transfer as much as possible of the precipitate from the dish to a weighed crucible or a very small light dish or Pyrex beaker. Dissolve the small amount of precipitate on the paper and that left in the dish in a small volume of hot water, and evaporate the solution in the crucible containing the bulk of the precipitate. Dry the residue to constant weight at 130° to 140°. Keep the crucible loosely covered to avoid loss by decrepitation. From the weight of potassium chloroplatinate obtained, calculate the weight and percentage of potassium chloride by using the factor 0.3056.[3] Save the weighed precipitate and the filtrate for the recovery of the platinum.

NOTE:

Smith and Shead[4] have shown that it is advantageous to convert the mixed chlorides to perchlorates by evaporation to dryness with perchloric acid and then to apply the chloroplatinate method in modified form. The perchlorates are dissolved in a small volume of hot water, alcohol is added, and then chloroplatinic acid until potassium is precipitated and an excess is present. Enough alcohol is then added to make its concentration 80 to 85 per cent by volume. The digested solution is cooled, the precipitate is filtered off, washed, and weighed as K_2PtCl_6 after drying at 300° to 350°. The advantages of the method are: Only enough chloroplatinic acid to react with the potassium need be added since sodium perchlorate is soluble in alcohol, stronger alcoholic solutions can be used than in the Fresenius method, the method is one of precipitation and not of semi-extraction, the potassium chloroplatinate can be dried at 350° to render it entirely water-free, and the theoretical factor can be used to calculate potassium.

---

[1] The reduction of the platinum is conveniently effected by metallic magnesium. See W. B. Hicks, J. Ind. Eng. Chem. *5*, 650 (1913); T. E. Keitt and H. E. Shiver, J. Ind. Eng. Chem. *10*, 219, 994 (1918); *11*, 1049 (1919).

[2] Eighty per cent alcohol by volume is prepared by mixing 5 volumes of 95 per cent alcohol with 1 volume of water. The specific gravity of the mixture should be 0.86.

[3] For calculating the weight of K_2O, use the value 0.1931 for the factor $\frac{K_2O}{K_2PtCl_6}$.

[4] G. F. Smith and A. C. Shead, J. Am. Chem. Soc. *54*, 1722 (1932).

✓ 2. ***The perchlorate method.*** The perchlorate method for the separation of potassium from sodium is based on the fact that potassium perchlorate is very slightly soluble in organic liquids such as anhydrous ethyl alcohol,[1] ethyl acetate, *n*-butyl alcohol,[2] or a mixture of the latter with ethyl acetate,[3] whereas sodium (and lithium) perchlorate is freely soluble in these. In applying these methods, the alkali chlorides are converted into the perchlorates by evaporation to dryness with perchloric acid, and the residue is dissolved in a minimum volume of water and precipitated by the addition of a large excess of solvent, or the dry residue is extracted with the organic solvent. The precipitated or undissolved potassium perchlorate is washed and then weighed after heating to 160° to 350°. Sodium and lithium can be determined in the filtrate if desired.

The butyl alcohol-ethyl acetate method.[4] It has been found by Smith[5] that a mixture of equal parts of anhydrous *n*-butyl alcohol and ethyl acetate is superior to other organic liquids for the separation of the insoluble alkali perchlorates (potassium, rubidium, and cesium) from the soluble (sodium and lithium). The method is an extraction method, i.e., the anhydrous perchlorates are extracted with the organic mixture. Sodium perchlorate is occluded by the potassium perchlorate so that it is necessary to dissolve the first residue in water, evaporate, and repeat the extraction. The potassium perchlorate weighed contains a little occluded sodium perchlorate, which compensates for a slight solubility loss of potassium (under working conditions at room temperature the solubility of potassium perchlorate in the butyl alcohol-ethyl acetate mixture is 1.0 mg. per 100 ml., corresponding to 0.6 mg. of potassium chloride). The separated potassium perchlorate must be heated to 350° before weighing to expel occluded water. The procedure requires the absence of ammonium salts and sulfates.

Procedure.

Reagents: *Perchloric acid.* 60 to 70 per cent; free from nonvolatile matter.

Normal butyl alcohol. Fractionally distil a C. P. product, and use the fraction boiling between 116° and 118° at 760 mm.

Ethyl acetate. The product must be anhydrous and free from ethyl alcohol and should have a purity of 99.7 to 100.0 per cent.

---

[1] G. P. Baxter and M. Kobayashi, J. Am. Chem. Soc. *39*, 249 (1917).

[2] G. F. Smith, J. Am. Chem. Soc. *45*, 2072 (1923).

[3] G. F. Smith and J. F. Ross, J. Am. Chem. Soc. *47*, 1020 (1925).

[4] G. F. Smith and J. F. Ross, *loc. cit.*

[5] G. F. Smith, J. Am. Chem. Soc. *47*, 762 (1925).

Dissolve the mixed alkali chlorides[1] of potassium and sodium (lithium) in a small volume of water in a 150 ml. Pyrex beaker, and treat with two to three times the equivalent quantity of pure perchloric acid (in any case not less than 1 ml. of 60 to 70 per cent acid). Evaporate to dryness on the hot plate (not above 350°). If there is any acid on the side walls, "brush" the beaker with a flame to remove it. Cool, dissolve the residue in water (2 or 3 ml. will generally suffice), and again evaporate to dryness on the hot plate. To the cool residue add 10 to 20 ml. of a mixture of equal parts of anhydrous *n*-butyl alcohol and ethyl acetate, and digest near the boiling point for two to three minutes. Cool the solution to room temperature, and decant the supernatant liquid through a weighed porcelain filter crucible. Wash three times by decantation with 3 to 5 ml. portions of butyl alcohol-ethyl acetate. Dissolve the residue in a minimum volume of hot water, evaporate to dryness, and extract as before, using 10 ml. of solvent. Then transfer the precipitate to the crucible, using a fine jet of the mixed solvent from a wash bottle. Wash the crucible and its contents approximately six times with 1 ml. portions of butyl alcohol-ethyl acetate. Dry the beaker, and brush any particles in it into the crucible. Place the crucible in an oven at 110° for ten minutes, and then heat covered at 350° for fifteen minutes in a muffle. Cool and weigh as $KClO_4$.

NOTES:

1. Anhydrous ethyl acetate (99.7–100 per cent) may be used instead of the mixed solvent in the above procedure. The solubility of potassium perchlorate in ethyl acetate is 1.3 mg. per 100 ml. at 25°. Although the solubility of sodium perchlorate in ethyl acetate (8.4 g. per 100 ml. at 25°) is less than in the mixed solvent (13.2 g. per 100 ml.), the solubility is still great enough to make ethyl acetate a suitable solvent, and good results are obtained in its use.

2. In the filtrate, sodium can be precipitated as the chloride, after the evaporation of the ethyl acetate, by the addition of a butyl alcohol solution of hydrogen chloride; the sodium chloride thus precipitated can be weighed as such or titrated with silver nitrate by Mohr's method. In the filtrate from the sodium chloride, lithium can be determined as the sulfate. For details see the paper of Smith and Ross.

The following figures, taken from the paper by Smith and Ross already cited, attest the accuracy of the method and show the error resulting from a single extraction of the mixed perchlorates:

KCl TAKEN	NaCl TAKEN	KCl FOUND		NaCl FOUND
g.	g.	1 extr. g.	2 extr. g.	(grav. after 2 extr. of K) g.
0.1293	0.1306	0.1305	0.1292	0.1306
0.1463	0.1349	0.1472	0.1462	0.1344
0.1416	0.1355	0.1427	0.1416	0.1350
0.2346	0.0318		0.2336	0.0316

---

[1] Nitrates, acetates, etc. may be used but not sulfates. Calcium and magnesium may be present.

Direct determination of sodium.

It is possible to determine sodium in the filtrate from the potassium chloroplatinate or potassium perchlorate precipitate by methods which will not be described here. Usually it is more convenient to precipitate sodium directly without the previous separation of potassium. The direct determination of sodium in the presence of the other alkali metals (except lithium) is based upon its precipitation as a slightly soluble triple acetate with uranyl ion having the general formula:

$$Na(C_2H_3O_2) \cdot M(C_2H_3O_2)_2 \cdot 3\,UO_2(C_2H_3O_2)_2 \cdot 6\,H_2O$$

in which M may be magnesium, zinc, nickel, or certain other divalent metals. It has been found that the triple acetates with zinc and magnesium[1] are the most satisfactory precipitation forms for sodium.

Determination of sodium as sodium uranyl zinc acetate.[2]

The solubility of sodium uranyl zinc acetate hexahydrate in water is fairly great, being 5.85 g. per 100 ml. of solution at 21°. It is evident, therefore, that a special precipitation procedure must be followed to separate sodium quantitatively. It has been found that sodium can be precipitated completely by adding a comparatively large volume of a strong solution of the reagent, uranyl zinc acetate, saturated with the sodium salt, to a very small volume of the alkali metal solution. The triple acetate separates almost immediately in the form of coarse crystals, but it is necessary to allow the solution to stand for an hour or so with occasional stirring to assure quantitative precipitation. The precipitate is collected in a filter crucible and washed with successive small portions of the reagent solution saturated with the triple salt. The adhering solution of the reagent is next washed out with 95 per cent alcohol saturated with sodium uranyl zinc acetate. Finally the precipitate is washed with acetone or ether to remove the alcohol, and a stream of air is drawn through the crucible to cause the evaporation of the former. The precipitate is weighed in the air-dry state as $NaC_2H_3O_2 \cdot Zn(C_2H_3O_2)_2 \cdot 3\,UO_2(C_2H_3O_2)_2 \cdot 6\,H_2O$. The very small calculation factor is of great advantage when a small amount of sodium must be determined but, on the other hand, limits the weight of sample that can conveniently be taken when potassium and sodium are present in similar amounts, so that an aliquot part may then have to be taken.

The water content of the dried triple acetate is slightly greater than corresponds to the hexahydrate The amount of foreign water ("zeolitic water," according to Schoorl[3]) depends upon the relative humidity of the atmosphere in which the precipitate is dried. Schoorl found the following water contents after drying at room temperature at various humidities:

---

[1] E. R. Caley and C. W. Foulk, J. Am. Chem. Soc. *51*, 1664 (1929); Caley, *ibid.* *52*, 1349, 4247 (1930).

[2] H. H. Barber and I. M. Kolthoff, J. Am. Chem. Soc. *50*, 1625 (1928).

[3] N. Schoorl, Rec. trav. chim. *59*, 305 (1940).

Relative Humidity Per Cent	Molecules of H_2O in Precipitate
0	6.17
0.34	6.45
0.68	6.53
0.94	6.64
0.98	6.80

The slightly high results due to foreign water are compensated by small solubility losses in the procedure. It may be mentioned that the hydrate water of the triple acetate is so firmly bound that it is not expelled when the precipitate is heated at 110°.

Lithium interferes in the determination since it also forms a slightly soluble triple acetate [1] with the uranyl zinc acetate reagent, and it must therefore be removed by appropriate methods before the precipitation of the sodium. Potassium does not interfere except when present in relatively large amounts. If more than 50 mg. of potassium chloride are present per ml. of solution to be precipitated, the solution must be diluted until the concentration does not exceed this value. Since the reagent must be added in the ratio of at least 10 ml. to 1 ml. of the alkali solution to precipitate sodium quantitatively, such dilution is unpractical when very much potassium is present, and it is better in such a case to remove most of the potassium by precipitation as the perchlorate in a 70 per cent alcohol solution by the addition of ammonium perchlorate.[2] Ammonium salts, magnesium, calcium, and barium may be present in reasonable amounts; strontium leads to high results.[3] Organic acids such as oxalic and tartaric interfere, as do anions, such as phosphate,[4] which give precipitates with the reagent. Sulfate must be absent when potassium is simultaneously present, since potassium sulfate is only slightly soluble in the reagent. Sulfates can be converted into chlorides by treatment with barium chloride.

The accuracy of the triple acetate method for sodium is about 0.5 per cent, i.e., 1 : 200.

Procedure.

Reagents: *Uranyl zinc acetate.* Prepare by mixing equal volumes of solutions (a) and (b), allowing to stand twenty-four hours, and then filtering off the precipitate of sodium uranyl zinc acetate usually formed from traces of sodium in the reagents.[5] Preserve the solution in a Pyrex bottle.

---

[1] By using a uranyl zinc acetate reagent of special composition, it is possible to determine lithium as $LiZn(UO_2)_3(C_2H_3O_2)_9 \cdot 6\, H_2O$ after separation from sodium by the extraction of the alkali chlorides with a suitable organic solvent. See C. C. Miller and F. Traves, J. Chem. Soc. *1936*, 1395.

[2] H. H. Barber and I. M. Kolthoff, J. Am. Chem. Soc. *51*, 3233 (1929).

[3] In the presence of much magnesium, calcium, etc. a double precipitation may be necessary. Cf. Miller and Traves, J. Chem. Soc. *1936*, 1390. Consult this paper for a method of determining sodium directly in a silicate after decomposition by the J. L. Smith procedure.

[4] Phosphate can be removed by treating the solution with zinc carbonate. See O. R. Overman and O. F. Garrett, Ind. Eng. Chem., Anal. Ed. *9*, 72 (1937).

[5] If no precipitate is formed, add a small amount of sodium chloride to saturate the precipitant with the triple acetate. The solution should be filtered and used at approximately the same temperature (preferably 20°) to avoid errors due to solubility changes.

Solution (*a*). Mix 10 g. of $UO_2(C_2H_3O_2)_2 \cdot 2\,H_2O$, 6 ml. of 30 per cent acetic acid, and 50 ml. of water, and warm to dissolve.

Solution (*b*). Mix 30 g. of $Zn(C_2H_3O_2)_2 \cdot 2\,H_2O$, 3 ml. of 30 per cent acetic acid, and 50 ml. of water, and warm to dissolve.

Ethyl alcohol saturated with sodium uranyl zinc acetate. Shake 95 per cent alcohol with pure sodium uranyl zinc acetate at room temperature until saturated.

Ether or acetone.

Dissolve a sample containing not more than 8 mg. of sodium and 25 mg. of potassium,[1] and free from the interfering substances mentioned above, in 1 ml. of water in a 50 ml. Pyrex beaker. Add 10 ml. of uranyl zinc acetate solution, mix, and allow to stand covered for one hour. Stir at intervals to insure complete precipitation; the triple salt tends to form supersaturated solutions. Filter off the precipitate in a filter crucible (Gooch, sintered glass, or porous porcelain), suck dry, and wash the precipitation beaker, crucible, and precipitate with five to eight 2 ml. portions of the reagent; drain the crucible well each time. Then wash five times with 2 ml. portions of the alcohol wash solution and finally with a few small portions of ether or acetone. Draw air through the crucible for a few minutes to volatilize the ether or acetone. Place the crucible in the balance case, and weigh after ten or fifteen minutes. It is advisable to let the crucible stand on the balance pan for ten minutes or so and then weigh again to be sure that the weight is constant. To find the weight of sodium multiply the weight of the precipitate by 0.01495.

Indirect determination of sodium or potassium.

Sodium or potassium can be determined by difference by obtaining the weight of the anhydrous mixed chlorides (or perchlorates) of the two metals and then finding (1) the amount of potassium present by the chloroplatinate or perchlorate method, or else (2) the amount of sodium by the triple acetate method. Evidently this indirect method is less accurate than the direct determination, since any error made in the direct determination of one alkali falls on the other obtained by difference. Nevertheless, the indirect determination of one alkali metal is frequently resorted to in practical analysis, and the results are quite satisfactory. When results of the highest accuracy are desired, it is advisable to determine both sodium and potassium in separate portions of sample by the methods described in the preceding pages.[2] If a check on the direct determinations of both elements is desired, the mixed chlorides can be weighed before the precipitations are made.

---

[1] If more potassium is present, add more water, so that the concentration of potassium is less than 25 mg. per ml., and then add reagent in the ratio of 10 ml. for each ml. of solution present.

[2] The sample (mixed chlorides, for example) may be dissolved in water and made up to a convenient volume (or weight), $\frac{1}{5}$ or $\frac{1}{10}$ of the solution taken for the sodium determination by the triple acetate method, and the remainder used for the determination of potassium. As long as the amount of sodium present is not very much less than that of potassium, a small fraction of the sample will serve for the estimation of sodium since the molecular weight of the triple acetate is so high.

When the indirect method for one alkali metal is applied, it is of course necessary first to remove all other metals in order to obtain the weight of the mixed potassium and sodium salts. The series of separations[1] finally leaves ammonium salts with the sodium and potassium. Generally these metals will be present as the chlorides. Ammonium chloride is removed by ignition at a low temperature. The temperature of the heating must be quite carefully regulated because sodium and potassium chlorides volatilize easily above their melting points. If the chlorides are not heated high enough, they retain water. Therefore they are heated just to the temperature of incipient fusion. The alkali sulfates are much less volatile than the chlorides and would be a more desirable weighing form were it not for the fact that the presence of sulfate is usually objectionable in the direct determination of either sodium or potassium.

PROBLEMS

1. What is the minimum volume of chloroplatinic acid solution containing 0.10 g. of platinum per ml. that should be taken to assure the conversion of a 0.200 g. mixture of sodium and potassium chlorides into the chloroplatinates? *Ans.* 3.34 ml.

2. A determination of potassium in a 0.500 g. sample by the chloroplatinate method yielded the result, 20.27 per cent K_2O. If the solubility loss in the procedure was 1.0 mg. of K_2PtCl_6, find the corrected K_2O value. *Ans.* 20.31 per cent.

3. The potassium chloroplatinate precipitate from a 0.7504 g. sample was reduced to metallic platinum by magnesium. If 0.1122 g. of platinum was obtained, what was the percentage of potassium in the sample?

4. A 0.2046 g. mixture of anhydrous sodium and potassium chlorides was dissolved in water and a one-tenth aliquot taken for the determination of sodium by the triple acetate method. If the sodium zinc uranyl acetate precipitate obtained weighed 0.2117 g., find the percentage of sodium and potassium in the mixture. *Ans.* 15.47 per cent Na, 31.82 per cent K.

5. A sample consisting of the mixed chlorides of sodium and potassium weighing 0.3575 g. yielded 0.1162 g. of $KClO_4$. What is the percentage of Na_2O and K_2O in the sample?

6. If a weighed precipitate of sodium zinc uranyl acetate contained 7 molecules of water of crystallization instead of the assumed 6 molecules, what would be the error in the sodium determination? *Ans.* + 12 parts per thousand.

7. In the determination of potassium by the chloroplatinate method, the use of 80 per cent alcohol by volume is called for. How many ml. of 95 per cent (by volume) alcohol are required for the preparation of 1 liter of this alcohol solution?

---

[1] See, for example, the determination of the alkalies in a rock, p. 748.

CHAPTER XXVII

ELECTROLYTIC DETERMINATIONS

In this chapter a brief description is given of the apparatus used in electroanalysis, and the application of electrolytic methods to quantitative analysis is illustrated by the electroanalytical determination of copper and the separation of copper and nickel.[1]

Apparatus.

Electrolysis unit. A setup such as that diagrammatically illustrated in Figure 75 is employed in making electrolytic determinations. There are required: (1) a source of direct current, (2) suitable resistances to permit regulation of the amperage and voltage, (3) an ammeter and voltmeter, (4) a motor for stirring, and (5) electrodes. A detailed description of the apparatus will not be given here because the setups will vary to a greater or lesser extent from one laboratory to another and will depend on particular requirements.

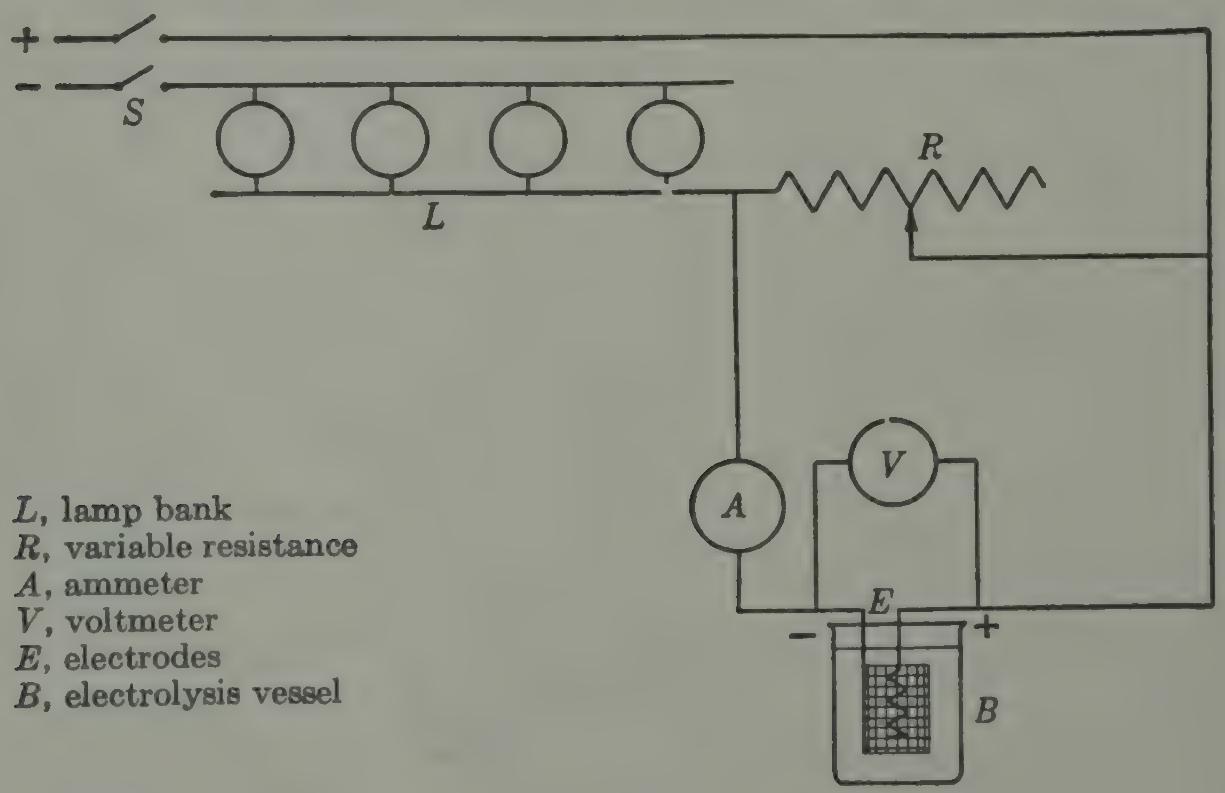


FIG. 75. Apparatus for electroanalysis.

---

[1] For an exhaustive treatment of electroanalysis, see Classen and Danneel, *Quantitative Analyse durch Elektrolyse.*

When available, a 110-volt direct current line furnishes the most convenient source of current. Alternating 110-volt current can easily be converted into direct current by the use of rectifiers. In case of necessity storage batteries may be used to supply the current. A motor for stirring is not essential but a great convenience because, as already stated (p. 158), a much higher current density can be employed when the electrolyzed solution is well stirred, and a much shorter time is then required for the electrolysis.

Electrodes. These are generally made of platinum.[1] The cathode may have the form of a gauze cylinder, a sheet cylinder, a perforated sheet cylinder, or a curved piece of gauze or sheet. The gauze cylinder (Fig. 76) is to be recommended especially. It permits free circulation of liquid during electrolysis and affords a good surface for deposition. In any case, the cathode must be so constructed that it presents a relatively large surface (p. 159). Sometimes a platinum dish is made to serve both as the cathode and the container for the solution to be electrolyzed.

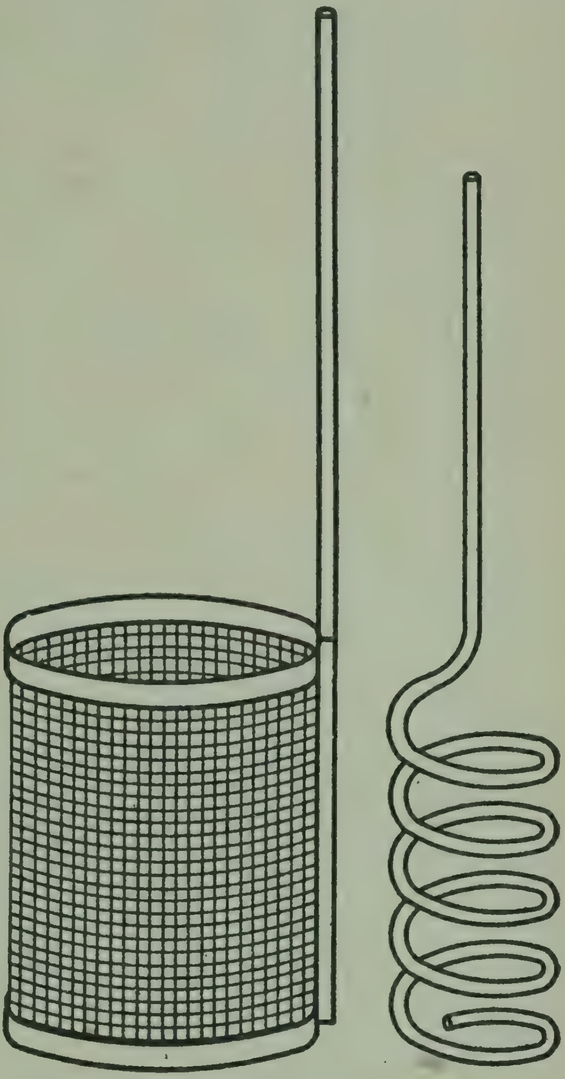


FIG. 76. Platinum cathode and anode.

The anode is often a stout platinum wire coiled into spiral form; but it may also be, for example, a gauze cylinder, this latter form being used when the deposit on the anode is to be weighed. The circulation of the solution during electrolysis may very conveniently be effected by rotating the anode (coiled form) through the agency of a motor,[2] the anode being attached to the collar of a vertical shaft and surrounded by a gauze-cylinder cathode. Alternatively the cathode, having a centered stem, can be rotated; or a glass propeller can be employed. When a platinum dish is used as cathode, the anode employed is made in the form of a disk or flattened spiral.

---

[1] *Cathodes* are not infrequently made of metals other than platinum or its alloys. Thus, cathodes of tantalum find considerable application in the deposition of certain metals (e.g., see B. Mears and P. R. Pine, Ind. Eng. Chem., Anal. Ed. *2*, 298 (1930) for the use of such cathodes in the determination of copper). Cathodes of gold and silver are satisfactory in some cases, and even copper cathodes are sometimes suitable, as in the determination of copper and zinc. *Anodes* are almost without exception made of platinum or its alloys.

[2] Stirring can also be effected by a current of air or electromagnetically.

Vessels. Tall-form beakers are commonly used to hold the solutions to be electrolyzed. To prevent loss through spraying, split watch glasses with a central hole (Fig. 77) are used for covering.

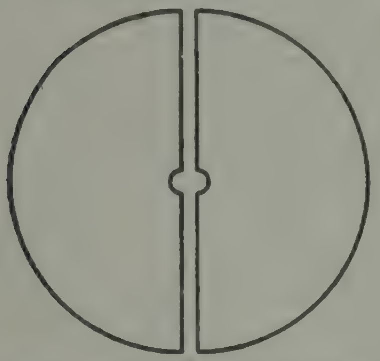


FIG. 77. Split watch glass.

Use and care of electrodes.

Before use, an electrode must be carefully cleaned to remove any previous deposit. Most metals can be removed by immersing the platinum electrode in 6 N nitric acid, rinsing with water, and reimmersing in boiling 6 N nitric acid, followed by a final washing in water. Cathodes with deposited nickel should first be treated with concentrated nitric acid. Lead dioxide may be removed from an anode by placing the latter in dilute nitric acid containing hydrogen peroxide.

It is important that the electrodes be free from grease, for otherwise an adherent deposit may not be obtained. Therefore an electrode should never be touched on the deposition surface with the fingers. Electrodes are easily rendered grease-free by heating them to redness in a flame. When such treatment is used, special care must be taken to see that no foreign metal is present on the platinum, for fear that an alloy may be formed.

The washed electrode is dried at 100° to 110° and weighed before electrolysis. When the electrolysis is finished, the electrode with its deposit is washed with water while in place and with the current still on. The electrode is then disconnected, rinsed with alcohol or, better, with acetone, and dried briefly at 100°. The drying at 100° should not be prolonged, for there may be danger of oxidizing the metal deposit (e.g., copper). After cooling to room temperature, the electrode with its deposit is weighed.

Electrolysis must never be conducted in acid chloride solutions because in such solutions corrosion of the platinum anode is very serious, leading not only to erroneous results (since the dissolved platinum is plated out on the cathode) but also to injury of the anode. In this connection it may be said that in the electrolysis of certain solutions it sometimes happens that a *slight* attack of the anode takes place and that in exact work account must be taken of the increase in weight of the cathode from this source. The occurrence of anode corrosion can be detected very simply by weighing the anode before and after electrolysis.

Certain metals (zinc, gallium, and bismuth) should not be deposited on platinum. These metals, especially zinc, appear to alloy with the platinum, or at least affect it in such a way that when they are dissolved off, the platinum surface is dulled or blackened. Injury to the platinum can be prevented in these cases by first coating it with copper and then depositing the metal on this surface.

Electrolytic determination of copper.

Method. It has been shown (p. 155) that copper can be quantitatively deposited from a dilute acid solution by the impression of an electromotive force of about 2 volts.

The reactions occurring at the electrodes are:

$$\left.\begin{array}{l} Cu^{++} + 2\,e \rightarrow Cu \\ (2\,H^+ + 2\,e \rightarrow H_2) \end{array}\right\} \text{(cathode)}$$

$$2\,OH^- \rightarrow \tfrac{1}{2}\,O_2 + H_2O + 2\,e \text{ (anode)}.$$

Conditions. The electrolysis is carried out in a solution acidified with both sulfuric and nitric acid. The acidity must not be too high, for then the deposition of copper may be incomplete or an unsatisfactory plate may be obtained. The beneficial effect of nitric acid in promoting the formation of a pure, firmly adherent coat of copper is explained by its depolarizing action at the cathode (p. 159):

$$NO_3^- + 10\,H^+ + 8\,e \rightarrow NH_4^+ + 3\,H_2O.$$

The reduction potential of the nitrate ion is lower than the discharge potential of the hydrogen, and therefore hydrogen is not liberated in the free state. It should be noted that the solution becomes less acid because of this reaction as the electrolysis proceeds, and that if it is unduly prolonged, electrodeposition of other metals such as nickel may occur. The nitrate ion may be supplied by adding nitric acid or ammonium nitrate. If nitric acid is used, care must be taken to see that it is free from nitrous acid because the latter will delay the deposition or tend to oxidize the copper and give rise to a deposit containing copper oxide. The oxides of nitrogen may be removed by boiling the nitric acid before adding it, or they may be destroyed in the electrolysis solution by adding urea:

$$2\,HNO_2 + (NH_2)_2CO \rightarrow 3\,H_2O + 2\,N_2 + CO_2.$$

Metals below copper in the electromotive series must of course be absent. Lead does not interfere because it is deposited as lead dioxide on the anode under the proper conditions of acidity. The presence of iron is objectionable. Ferric iron interferes with the deposition; and, moreover, when reduced by the current to the ferrous condition, it may reduce nitrate to nitrous acid when the acidity is high. However, very small amounts of iron are permissible. The deposit of copper should be a smooth adherent coat of salmon-pink color. If it is dark, the presence of metals other than copper is indicated. Spongy deposits result from the use of too high current densities or improper acidity and absence of nitrate ion.

Procedure. The following directions apply to the determination of copper in a solution free from the interfering substances mentioned above.[1] In a 150 ml. beaker prepare a solution containing 0.2 to 0.25 g. of copper in 100 ml. Add 2 ml. of concentrated sulfuric acid and 1 ml. of concentrated nitric acid (the latter freshly boiled to remove oxides of nitrogen). Clean the electrodes (p. 422), dry and weigh the gauze cathode, and then attach the electrodes, having the source of current disconnected. Be sure that the cathode is connected to the negative terminal. If a rotating anode is used, see that it can rotate without coming into contact with the cathode at any point. Raise the beaker into position, and adjust its height so that the electrodes extend nearly to the bottom of the beaker and the cathode is nearly but not entirely covered by the solution. The beaker should be placed on a wooden pedestal or tier of blocks, so that it can be easily lowered away from the electrodes at the end of the electrolysis. Cover the beaker with a split watch glass; and with all the resistance in, so that only a small current will flow, close the circuit, and proceed as in (1) or (2), depending on whether or not stirring is used.

(1) *Electrolysis without stirring.* Decrease the resistance until a current of approximately 0.5 ampere flows, as indicated by an ammeter in the circuit, and electrolyze overnight, using an applied potential of 2 volts[2] or more.

Alternatively, use a current of about 1.5 amperes, and electrolyze for three hours.

---

[1] For instructional purposes a sample of non-effloresced recrystallized copper sulfate pentahydrate is an excellent one when it is desired to work with a previously known amount of copper; as an "unknown," an intimate mixture of finely divided copper sulfate and, say, potassium sulfate will serve, or a copper-nickel alloy may be used by following the directions given on p. 426 without regard to nickel if it is not desired to determine the latter metal.

[2] A single lead accumulator may be used as a source of current (p. 155).

(2) *Electrolysis with stirring.* Start the motor driving the anode or glass propeller, and adjust its speed so that the solution is vigorously stirred without there being any danger of mechanical loss of liquid. Regulate the resistance to give a current of 3 to 4 amperes; the voltage across the electrode terminals should be 2 to 4 volts (not above the latter figure in the presence of nickel). Continue the electrolysis for about forty-five minutes, or until the blue color of the copper has entirely disappeared.

Regardless of whether procedure (1) or (2) is used, rinse off the cover glass into the beaker when it is judged that the electrolysis is complete, and add more water, if necessary, to bring the level of the solution above the top of the cathode. Continue the electrolysis for one-half hour if procedure (1) is used, or for a quarter of an hour without stirring if procedure (2) is followed (in the latter case reduce the amperage to 0.5 to 1). If at the end of this time no copper deposit has appeared on the freshly immersed surface of the cathode, it may be assumed that the deposition is complete. If a coat of copper does form, continue the electrolysis as long as may be judged necessary, and again test as before by adding a little more water and seeing whether a further deposit is formed on the stem of the cathode.

When the electrolysis is complete, slowly lower the beaker (or raise the electrodes) while directing a stream of water from the wash bottle against the exposed part of the cathode. Do not break the current until the cathode is entirely out of the solution and has been thoroughly washed. Any acid solution allowed to remain on the deposit will partially dissolve it. Finally dip the cathode into a beaker of water to insure the removal of any soluble substances, and then rinse it with successive portions of alcohol or acetone to remove water. Place the cathode in an oven heated to 100°, and remove after two to three minutes. Cool to room temperature and weigh. Calculate the percentage of copper.[1]

Electrolytic separation and determination of copper and nickel.

The theory of the separation of metals by electrolysis has been discussed in Chapter X (pp. 156 *et seq.*).

---

[1] In the most exact work the cold electrolyzed solution should be saturated with hydrogen sulfide to precipitate any copper remaining in solution, the precipitate washed with colorless ammonium sulfide, and then ignited to cupric oxide in a porcelain crucible. The copper corresponding to the weighed residue is added to the weight of the electrolytic deposit to obtain the entire amount of copper present in the sample. Of course, metals that give sulfides insoluble in the acid solution must be absent, or the copper precipitate must be examined for them.

Method. Copper is separated from nickel by electrodepositing the former in a sulfuric-nitric acid solution under a potential difference of 2 to 4 volts, the solution being stirred; under these conditions, nickel does not separate. The solution from which copper has been separated is evaporated and heated to fumes of sulfuric acid to expel nitric acid, which would interfere in the deposition of nickel. The residue is dissolved in water, and an excess of ammonium hydroxide is added. Electrolysis of this solution, in which nickel is present as the complex ion $Ni(NH_3)_4^{++}$, deposits the nickel on the cathode.

Conditions. The quantitative separation of copper from nickel by electrolysis demands the deposition of the former metal from a strongly acid solution with a regulated potential difference across the electrodes; failure to pay proper attention to these points may result in the partial deposition of nickel and erroneous results for both metals.

Nickel cannot be quantitatively deposited from a weakly acid solution. From a solution containing an excess of ammonium hydroxide, together with ammonium sulfate, the metal can be plated out completely with great ease. The existence of nickel in this solution as $Ni(NH_3)_4^{++}$ is conducive to the formation of a very satisfactory plate (p. 159). The electrolysis is best made in a solution of the sulfates, but chlorides can be used. Nitrates cause difficulties and should be absent. Metals, such as ferric iron, which give precipitates with ammonium hydroxide should be removed prior to the electrolysis, because the precipitates are occluded to a greater or lesser extent by the metal deposit. Elements such as silver and zinc which form soluble ammonio complexes must be absent as they are likewise deposited. Ferrous salts are very objectionable. Cobalt is deposited with the nickel, but the last traces of the former metal require special measures for quantitative deposition.

The electrolysis should not be unduly prolonged because the anode is slightly attacked.

Procedure for the determination of copper and nickel in a copper-nickel alloy.[1] The following directions apply to the separation and determination of the metals named in an alloy which contains in addition only a *small* amount of iron. Such alloys are monel metal and nickel-copper coinage alloys (e.g., U. S. five-cent piece). The iron must be removed after the deposition of the copper by double precipitation with ammonium hydroxide (p. 317).

---

[1] Willard and Furman, *Elementary Quantitative Analysis.*

If the alloy is greasy, boil it with 6 *N* sodium hydroxide solution, wash with water, and dry. Weigh out 0.5 g.[1] of sample into a 150 ml. beaker, and dissolve in a mixture of 10 ml. of water, 1 ml. of concentrated sulfuric acid, and 2 ml. of concentrated nitric acid. Boil out the oxides of nitrogen, and dilute to 100 ml.

Determination of copper. Proceed as directed on page 424, using either the slow or rapid method of electrolysis.

Determination of nickel. Nitric acid and iron must first be removed.

Evaporate on a low-temperature hot plate the solution from which copper has been deposited, and then heat at a higher temperature until fumes of sulfuric acid appear. Cool the residue, and add 25 ml. of water with care. Precipitate the iron (now in the ferric condition) by the addition of about 10 ml. of 1 : 1 ammonium hydroxide in excess. Filter through a small paper filter and catch the filtrate in a 150 ml. beaker. Wash the precipitate three times with water, place the original beaker under the funnel, dissolve the hydrous ferric oxide in a little hot 1 : 5 sulfuric acid, and wash the paper with water. Again precipitate the iron with the same large excess of ammonia, and filter through the same paper. Wash the precipitate, collecting the washings in the beaker containing the filtrate and washings from the first precipitation. Discard the precipitate.

Add 15 ml. of concentrated ammonium hydroxide to the ammoniacal nickel solution, dilute to 100 ml., and electrolyze with or without stirring, using the current strengths specified on pp. 424–25 for the deposition of copper. Use a potential of 3 to 4 volts. Wash the nickel deposit as directed under the determination of copper, dry, and weigh. Calculate the percentage of nickel.

Clean the cathode as described on page 422.

---

[1] If the alloy is in inconveniently large pieces, take a larger sample, dissolve in correspondingly more acid, dilute with water to the mark in a volumetric flask, and take a suitable aliquot portion for the analysis.

VOLUMETRIC ANALYSIS

CHAPTER XXVIII

GENERAL DISCUSSION OF VOLUMETRIC ANALYSIS

Definition.

In gravimetric analysis the constituent being determined is quantitatively precipitated with an *excess* of *precipitating agent;* after washing, the precipitate is *weighed* as such or after conversion into a suitable weighing form.

In volumetric analysis the solution of the substance being determined is treated with a solution of a suitable reagent of *exactly known concentration.* The addition of reagent is continued until the amount of reagent added is *equivalent* to the *amount of substance to be determined, no excess of reagent* being used in general.

The solution of exactly known concentration is called the *standard solution;* it *contains a definite number of equivalents of reagent per liter.* It is added from a *buret* to the solution containing the sample, thus allowing the *volume of standard solution* added to the solution of the substance to be determined. The operation itself is called a *titration,* and the substance to be determined is *titrated.* Thus *in a titration standard solution is added from a buret until the amount added is equivalent to that of the substance sought.* This point is called the *equivalence point* or *theoretical end point.* An auxiliary reagent known as an *indicator* is added to the system to show the point at which the amount of reagent added is equivalent to that of the substance to be determined. After the reaction between the standard solution and the substance titrated is virtually complete, the *indicator gives a visual change* (either a color change or formation of turbidity) *in the liquid titrated.* The point at which this change takes place is called the *end point of the titration.* The end point does not necessarily coincide with the equivalence point, the latter being the *theoretical* end point. One should always endeavor to select an indicator such that the difference between the equivalence point and end point is as small as possible. If the properties of the indicator and the system titrated are known, it is possible to calculate the difference in location of the equivalence and end point expressed in the percentage of the substance determined. The difference is the *titration error;* it can be determined experimentally and is called the indicator blank. Later a few simple examples of the derivation of the titration error will be given.

Ordinarily, a proper amount of the indicator is added to the system to be titrated, and the color change is observed in the solution. Such indicators are called *internal* or *inside indicators.* In certain cases an interaction between the indicator and the system titrated takes place before the end point is reached. Under these conditions the end point appears too early. This, for example, occurs in the titration of phosphate with uranyl acetate when potassium ferrocyanide is used as indicator. The uranyl ferrocyanide, which has a red-brown color, is so slightly soluble that potassium ferrocyanide reacts with the uranyl ions before the end point is reached. A good result can be obtained only if small portions of the supernatant liquid or of the filtrate are tested at intervals on a spot plate or a piece of filter paper with potassium ferrocyanide as an indicator. The latter then functions as an *external* or *outside* indicator. Wherever possible the use of internal indicators is naturally preferred over that of external ones.

The main differences then between a gravimetric and a volumetric procedure are that in the latter the amount of reagent is accurately measured, that only an amount equivalent to that of the substance to be determined is added, and that most reactions which take place quantitatively can be made the basis of a titration. In gravimetric procedures we are mainly limited to the formation of precipitates, whereas in volumetric analysis any type of reaction can be used.

Classification of volumetric methods.

1. *Methods based upon the combination of ions.*

$$\text{(a)} \qquad \left\{\begin{array}{c} H^+ + OH^- \rightleftarrows H_2O \\ H^+ + A^- \rightleftarrows HA \\ B^+ + OH^- \rightleftarrows BOH. \end{array}\right.$$

Use is made of the above reactions in the volumetric determination of substances behaving like acids or bases. Acids and salts of very weak bases can be titrated with a standard base; bases and salts of very weak acids can be titrated with a standard acid. In the latter case we speak of *acidimetry,* in the former of *alkalimetry.*

(b) $$Ag^+ + Cl^- \rightleftarrows AgCl$$
$$3\ Zn^{++} + 2\ K_4Fe(CN)_6 \rightleftarrows K_2Zn_3[Fe(CN)_6]_2 + 6\ K^+.$$

Methods in which use is made of the formation of precipitates are usually called *precipitation processes.* One of the most common reagents is *silver nitrate.* Volumetric procedures based upon the use of this reagent are often called *argentimetric* (or *argentometric*) methods.

(c) $$2\ CN^- + Ag^+ \rightleftarrows Ag(CN)_2^-.$$

Application is also made of the fact that the substance to be determined can sometimes be quantitatively transformed into a soluble complex, or into a slightly dissociated compound:

$$2\ Cl^- + Hg^{++} \rightleftarrows HgCl_2.$$

2. *Methods based upon the transfer of electrons.*

Oxidation-reduction reactions. Extremely important applications of oxidation-reduction reactions are made in volumetric analysis.

Some of the well-known and frequently used oxidizing agents are: *potassium permanganate, ceric sulfate, potassium dichromate, iodine, potassium iodate* and *bromate,* and *bromine.*

Frequently used reducing agents are: *sodium thiosulfate* (for the measurement of iodine), *ferrous sulfate, arsenic trioxide, titanous chloride,* and *chromous chloride.*

Limitations of volumetric methods.

Not every chemical reaction can serve as the basis of a titration. The following conditions at least must be fulfilled:

1. The reaction between the substance to be determined and the reagent should occur with great speed. This condition is satisfied by all reactions used in acidimetry and alkalimetry; the same is also the case with reactions in which slightly dissociated compounds and complex compounds are formed. In precipitation reactions the precipitate does not always separate instantaneously (see Chapter VII on the formation of precipitates). The silver halides are formed almost instantaneously; microcrystalline precipitates such as barium sulfate and lead sulfate separate more slowly, especially from dilute solutions. In such cases addition of alcohol may have a favorable effect, since as a rule it decreases the solu-

bility of slightly soluble inorganic salts and consequently increases the speed of precipitation.

Various oxidation-reduction reactions do not take place instantaneously. In such cases the addition of a suitable *catalyst* (see p. 33) increases the speed of reaction. When the reaction velocity is slow or when the end point cannot be detected in a simple way, a known excess of the reagent is often added, and the excess is back-titrated with a suitable standard solution after the first reaction is complete.

2. The substance to be determined should react stoichiometrically with the reagent, and no side reactions should occur. Sometimes it is possible to develop an *empirical* method in cases in which side reactions occur. In such cases the conditions under which the procedure is carried out must be exactly defined and the directions followed very closely. Such a method is used, for example, in the determination of reducing sugars with an excess of an alkaline copper solution. Quite generally, however, such empirical methods are not to be recommended.

3. Other substances present in the solution should not react or interfere with the main reaction. A reducing agent frequently reacts slowly with atmospheric oxygen so that its solution is stable for a comparatively short time only. However, in the titration of reducing agents it is often found that the main reaction taking place promotes the reaction between the reducing substance and oxygen. We then speak of an *induced* reaction. A solution of sulfite or bisulfite, for example, is oxidized by air, this oxidation being induced by the reaction between sulfite or bisulfite and iodine.

4. An indicator should be available for the detection of the end point. If no suitable indicator is available for the detection of the end point, the latter very often can be found by the application of physico-chemical methods. As such the change of the *potential of a certain electrode* during the course of a titration (*potentiometric titration*), the change of the *electrical conductivity* of the solution during the titration (*conductometric titration*), or the change of the *current upon electrolysis* of the solution being titrated (*amperometric titration*) will serve for finding the location of the equivalence point (p. 501).

Equivalent weight. Normality.

The *equivalent weight*, the *gram equivalent*, or the *equivalent* of a substance is the weight in grams *which in its reaction* correspond-to a gram atom of hydrogen, or of hydroxyl, or half a gram atom of oxygen, or a gram atom of a univalent ion. The equivalent weight is not a constant as the molecular weight is but depends upon the reaction in which the standard solution is used. This will be clear from the following examples.

In acid-base titrations it is always very simple to derive the equivalent weight. In the titration of monovalent bases and acids an equivalent is equal to a mole:

$$H^+ + Cl^- + Na^+ + OH^- \rightarrow Na^+ + Cl^- + H_2O.$$

With polyvalent acids and bases the equivalent is a variable. Sulfuric and oxalic acids, for example, are always titrated as dibasic acids, and therefore the equivalent of these is one half of the molecular weight. The case of phosphoric acid, however, is different; this acid can be titrated as a monobasic or a dibasic acid, and in the presence of much calcium chloride as a tribasic acid:

$$H_3PO_4 + OH^- \rightarrow H_2PO_4^- + H_2O \qquad (1)$$

$$H_3PO_4 + 2\,OH^- \rightarrow HPO_4^{=} + 2\,H_2O \qquad (2)$$

$$H_3PO_4 + 3\,OH^- \rightarrow PO_4^{\equiv} + 3\,H_2O. \qquad (3)$$

In the titration according to equation (1) the equivalent is equal to one mole, in (2) to $\frac{1}{2}$ mole, and in (3) to $\frac{1}{3}$ mole.

In precipitation and complex-formation analysis also we may read directly from the reaction equation the relation between the molar and the equivalent weight. If cyanide is titrated with silver according to the Mohr method, the equivalent of the former is equal to a mole:

$$Ag^+ + CN^- \rightarrow AgCN.$$

If the cyanide is titrated according to the method of Liebig, the end point is reached when the following reaction is complete:

$$Ag^+ + 2\,CN^- \rightarrow Ag(CN)_2^-.$$

In this case the equivalent of cyanide is two moles.

In oxidation-reduction reactions the equivalent of a substance is that part of a mole which in its reaction corresponds to the removal of one half of a gram atom of oxygen or the combination with one gram atom of hydrogen or any other univalent element. Quite generally the easiest way to find the equivalent is to determine the change in the *state of oxidation* in the reaction.

Example: In the titration of ferrous iron to ferric iron with any oxidizing agent, the state of oxidation of the iron changes from two to three:

$$Fe^{2+} \rightarrow Fe^{3+}.$$

The equivalent of ferrous iron in this case is equal to one mole. If metallic iron, however, is determined by oxidation to the ferric state:

$$Fe^{\circ} \rightarrow Fe^{3+},$$

the equivalent is equal to $\frac{1}{3}$ of a mole.

Copper can be titrated iodometrically by making use of the following reactions:

$$2\,Cu^{++} + 4\,I^- \rightarrow 2\,CuI + I_2 \tag{1}$$
$$2\,S_2O_3^{=} + I_2 \rightarrow S_4O_6^{=} + 2\,I^-. \tag{2}$$

Considering the fact that one copper ion reacts with two iodide ions (equation 1), one might at first infer that the equivalent of copper is one-half mole. However, in this titration use is made of the fact that the liberated iodine is measured (with sodium thiosulfate), and accordingly it is seen that one mole of copper corresponds to one equivalent of iodine and that the equivalent of copper therefore is one mole. Equation (2) shows us that the equivalent of sodium thiosulfate in iodometric titrations is the molecular weight.

In general, it is not necessary to write the entire balanced equation in order to find the equivalent weight; it is much simpler to write down the change in the state of oxidation. If permanganate is used as an oxidizing agent in acid medium, it is reduced to manganous ions:

$$MnO_4^- \rightarrow Mn^{2+}$$

or

$$Mn^{7+} \rightarrow Mn^{2+}.$$

This corresponds to a change of five units in the state of oxidation of the manganese. The equivalent of permanganate in acid medium, therefore, is $\frac{1}{5}$ of a mole. If used in neutral medium, the permanganate is reduced to MnO_2:

$$MnO_4^- \rightarrow MnO_2$$
$$Mn^{7+} \rightarrow Mn^{4+},$$

and the equivalent then is $\frac{1}{3}$ of a mole.

If a substance A is allowed to react with another substance and the reaction product is titrated, the equivalent weight of substance A is found from the equation which represents the titration of the reaction product. For example, iodate in acid medium reacts with iodide to form iodine:

$$IO_3^- + 5\,I^- + 6\,H^+ \rightarrow 3\,I_2 + 3\,H_2O.$$

If this titration were carried out directly with standard iodide solutions (e.g., potentiometrically), the equivalent weight of iodate would be equal to $\frac{1}{5}$ of the molecular weight. However, ordinarily the iodine formed in the above reaction is titrated with thiosulfate; and the equivalent of iodate, therefore, is $\frac{1}{6}$ of a mole.

Instead of speaking of the state of oxidation, it is also possible to define the equivalent weight as a function of the number of electrons transferred in the oxidation-reduction reaction. Any oxidation or reduction involves the transfer of electrons. The equivalent weight of a substance then is equal to the molecular weight divided by x, the number of electrons which one mole of the substance loses or gains in the reaction.

$$\text{Eq. Wt.} = \frac{M}{x}$$

Examples:

$$Fe^{++} \rightleftharpoons Fe^{+++} + e \qquad \text{Eq. Wt.} = \frac{Fe}{1}$$

$$Sn^{++} \rightleftharpoons Sn^{++++} + 2\,e \qquad \text{Eq. Wt.} = \frac{Sn}{2}$$

$$Fe(CN)_6^{\equiv\,-} \rightleftharpoons Fe(CN)_6^{\equiv} + e \qquad \text{Eq. Wt.} = \frac{Fe(CN)_6}{1}$$

$$As^{+++} \rightleftharpoons As^{+++++} + 2\,e \qquad \text{Eq. Wt.} = \frac{As}{2}.$$

The same considerations hold for oxidizing agents containing oxygen:

$$MnO_4^- + 8\,H^+ + 5\,e \rightarrow Mn^{++} + 4\,H_2O \qquad \text{Eq. Wt.} = \frac{MnO_4}{5}$$

$$MnO_4^- + 4\,H^+ + 3\,e \rightarrow MnO_2 + 2\,H_2O \qquad \text{Eq. Wt.} = \frac{MnO_4}{3}$$

$$Cr_2O_7^= + 14\,H^+ + 6\,e \rightarrow 2\,Cr^{+++} + 7\,H_2O \qquad \text{Eq. Wt.} = \frac{Cr_2O_7}{6}$$

$$VO_4^{\equiv} + 6\,H^+ + e \rightarrow VO^{++} + 3\,H_2O \qquad \text{Eq. Wt.} = \frac{VO_4}{1}.$$

The student must clearly understand that the equivalent of a substance is not a fixed quantity but depends upon the kind of reaction in which it takes part. One cannot answer offhand, for example, the following question: What is the equivalent weight of potassium iodate? If potassium iodate is determined by precipitation as silver iodate:

$$IO_3^- + Ag^+ \rightarrow AgIO_3, \text{ the Eq. Wt.} = \frac{KIO_3}{1}.$$

If it is reduced to iodine:

$$IO_3^- + 5\,I^- + 6\,H^+ \rightarrow 3\,I_2 + 3\,H_2O, \text{ the Eq. Wt.} = \frac{KIO_3}{6}.$$

If it is used as an oxidizing agent in 6 N hydrochloric acid, the iodate is reduced to ICl:

$$IO_3^- + 2\,I^- + 3\,Cl^- + 6\,H^+ \rightarrow 3\,ICl + 3\,H_2O, \text{ the Eq. Wt.} = \frac{KIO_3}{4}.$$

In the last case the equivalent weight of iodide is $\frac{I}{2}$, since it is oxidized according to the electrochemical equation:

$$I^- \rightarrow I^+ + 2\,e$$
$$(ICl \rightarrow I^+ + Cl^-).$$

The number of equivalents of a substance dissolved in one liter of solution determines the *normality* (N) of the solution. If one equivalent is present in one liter, the solution is 1 N; if 0.05 equivalent is present, the solution is 0.05 N or $\frac{1}{20}$ N, etc.

The expression of the concentration of a solution in terms of normality may be ambiguous. If we are dealing with normal solutions of hydrochloric, sulfuric, and oxalic acids, of silver nitrate, iodine, and arsenic trioxide, the normality refers to the most common reactions in which these substances take part.

However, if the normality of a solution of ferric chloride, potassium ferrocyanide, or iodic acid is given, it is impossible to state what the molecular concentration is, unless the reaction is given to which the normality refers. A 1 N ferric chloride solution may be 1 M: $Fe^{+++} \rightleftharpoons Fe^{++} + e$,

or $\frac{1}{3}$ M: $Fe^{+++} + 3\,OH^- \rightleftharpoons Fe(OH)_3$.

A 1 N potassium ferrocyanide solution may be 1 M:

$$Fe(CN)_6^{----} \rightleftharpoons Fe(CN)_6^{---} + e$$

or $\frac{1}{4}$ M: $Fe(CN)_6^{----} + 2\,Pb^{++} \rightleftharpoons Pb_2Fe(CN)_6$.

In such cases it is best to indicate on the label of the bottle the molarity of the solution with the normality, for example, in the following way:

$$1\,N\ K_4Fe(CN)_6\left(\frac{M}{1}\right) \text{ or } 1\,N\ K_4Fe(CN)_6\left(\frac{M}{4}\right).$$

Calculations in volumetric analysis.

The calculations of volumetric analysis are always very simple, since at the end point the number of equivalents of standard solution used is equal to the number of equivalents of the substance titrated.

EXAMPLES: A weighed amount, a grams, of the substance to be determined is dissolved and titrated. V_1 ml. of standard solution of normality N are used to reach the end point. What is the percentage of the substance titrated in the unknown?

One liter of the standard solution contains N equivalents. Therefore in V_1 ml. there are $V_1 \frac{N}{1000}$ equivalents. If the equivalent weight of the substance titrated is E, a grams of the unknown contain $\frac{V_1NE}{1000}$ grams of the substance titrated, and the percentage is $\frac{V_1NE}{1000} \cdot \frac{100}{a} = \frac{V_1NE}{10\,a}$. Often a weighed amount, a grams, of the substance to be titrated is dissolved and made up to a certain volume in a volumetric flask, and an aliquot part of this solution is then pipetted out. If, for example, 500 ml. of solution are prepared and 25 ml. are titrated, the above expression becomes:

$$\text{Percentage} = \frac{V_1NE}{10\,a} \times \frac{500}{25} = \frac{V_1NE}{10\,a} \cdot 20.$$

In the standardization of a solution (see next paragraph) an exactly weighed amount, say b grams, of the standard substance with the equivalent weight E_s is dissolved and titrated with the solution. V_1 ml. of the latter are used to reach the end point. What is the normality, N? b grams of the standard substance correspond to $\frac{b}{E_s}$ equivalents.

Therefore
$$\frac{V_1N}{1000} = \frac{b}{E_s}$$
$$N = \frac{1000\,b}{V_1E_s}.$$

If the normality, N_1, of a solution is determined by titrating a certain volume, V_1 ml., with a solution of a known normality, N_2, and V_2 ml. of the latter are used to reach the end point, we have the relation:

$$V_2N_2 = V_1N_1$$
$$N_1 = N_2 \frac{V_2}{V_1}.$$

The student should not make the calculations more involved than is necessary. If, for example, 25 ml. of a ferrous iron solution require 20 ml. of 0.125 N potassium permanganate for titration, there are present in the former $20 \times 0.125 \times \frac{55.84}{1000}$ grams of ferrous iron. The authors have found that a student often calculates the number of grams of permanganate used in the titration, then states that one mole of $KMnO_4$ corresponds to 5 moles of Fe^{++}, etc. This complicated way of computation, although leading to the same result, is entirely unnecessary and is to be considered wrong. The concept of normality has been introduced because it allows the calculation to be made with equivalents and not with grams and moles.

Preparation of standard solutions.

Solutions of definite normality can be prepared very simply when the substance that is to be dissolved is available in a pure state. Solutions of exactly known normality are then obtained by weighing out an equivalent or fractional part of it and making up the solution to a known volume. In this way standard solutions of potassium dichromate, sodium oxalate, oxalic acid, potassium biiodate, potassium biphthalate, sodium carbonate, borax, potassium iodate, potassium bromate, iodine, silver nitrate, alkali chlorides, and other substances may be prepared.

Such a direct preparation of a standard solution is not always possible. In the case of substances that cannot be obtained in a pure form, like most alkali hydroxides and various inorganic acids, solutions of approximately known normality are first prepared and standardized. If in such cases solutions are needed that are as close as possible to exactly 0.1 *N*, 0.5 *N*, etc., it is best to prepare, say, 1.2 liters of a solution of slightly higher normality. After standardization one can easily calculate what quantity of water, when added to one liter of the stronger solution, will bring it to the desired normality. The contraction in the process may usually be neglected. It is necessary to check the calculated normality by another standardization after the dilution.

The standard solutions should be kept in such a way that they do not change their titer on standing (see the practical part).

Use of primary standard substances.

Standardization. The standardization of a solution in general requires a higher degree of accuracy than an ordinary volumetric determination An error in the standardization recurs in all of the analyses that are made with the solution and therefore will add itself to the other errors.

For ordinary purposes one may be content with an accuracy of 0.1 per cent in the standardization, and it should be realized that this accuracy is not always easy to attain.

The following conditions must be fulfilled in a standardization:

1. In the first place, a suitable primary standard substance must be available. Such a substance should fulfill the following requirements: It must be easy to obtain, to purify and dry, and to preserve in a pure state. The substance must not be so hygroscopic that it takes up water during weighing. It must be capable of being tested for impurities by qualitative tests of known sensitivity. In general, the total amount of impurities in a primary standard should not be greater than 0.01–0.02 per cent. Each newly prepared primary standard must be subjected to severe tests of purity.

It is desirable that standard substances have a high equivalent weight in order that the weighing error may be insignificant (see below). The reaction with the standard solution must be stoichiometric. The error in the determination of the end point (titration error or indicator blank) must be negligible or easy to determine exactly experimentally.

The most important primary standard substances are considered in the practical part of this book. In certain cases it is permissible to use an impure substance as a standard (secondary standard substance) if the amount of the active material is exactly known.

Various attempts have been made to find *universal* primary standard substances which can be used for the standardization of different solutions employed in the various groups of volumetric analysis. Potassium acid iodate, $KH(IO_3)_2$, approaches this ideal more or less. It can be used for the determination of the titer of standard base:

$$KH(IO_3)_2 + NaOH \rightarrow KIO_3 + NaIO_3 + H_2O,$$

and of sodium thiosulfate,

$$KH(IO_3)_2 + 10\ KI + 11\ HCl \rightarrow 6\ I_2 + 6\ H_2O + 11\ KCl.$$

It can be reduced with pure sulfurous acid to iodide; and if the excess of the reducing acid is boiled off, a solution of iodide of exactly known concentration is obtained which may be used for the standardization of silver nitrate and permanganate solutions (p. 572).

Oxalic acid, $(COOH)_2 \cdot 2\ H_2O$, is used as a primary standard for the standardization of bases and permanganate. Sodium oxalate serves as a primary standard for the standardization of acids and permanganate. In the former case it is transformed into sodium carbonate by heating:

$$Na_2C_2O_4 \rightarrow Na_2CO_3 + CO.$$

Arsenic trioxide is used for the standardization of iodine, potassium permanganate, and ceric sulfate solutions.

2. The weight of the standard substance used should not be too small. Two weighings are involved in every determination. If the error of an ordinary analytical weighing is taken as 0.1 mg., then for every standardization at least 200 mg. of standard substance must be taken, if the error of weighing is not to exceed 0.1 per cent. For this reason standard substances with a high equivalent weight should be selected, if possible.

Potassium iodate, as a primary standard, has the disadvantage of a small equivalent weight (35.66). If, for example, 0.1 *N* thiosulfate is to be standardized with it and if 40 ml. of the latter are used, the corresponding weight of potassium iodate is only about 0.14 g. In such instances it is more advantageous to work with a solution of exactly known content. In the preparation of a liter of 0.1 *N* potassium iodate, 3.566 g. are used. An error in weighing amounting to 0.2 mg. corresponds to a relative error of 0.006 per cent and hence does not come into consideration at all. The allowable error of a liter volumetric flask is about 0.2 ml., corresponding to 0.02 per cent, and that of a 50 ml. pipet amounts to 0.07 per cent. Therefore, if we use 50 ml., the instrumental errors will be smaller than 0.1 per cent. In the standardization of very dilute solutions (0.025 *N* or weaker), an accuracy of 0.1 per cent is no longer obtainable by weighing out the primary standard directly, and here an exactly measured volume of a solution of exactly known content of the primary standard should be used.

3. The volume of standard solution used in the standardization should not be too small, if the result is not to be too greatly affected by the errors of reading and drainage. If each reading of the buret is subject to an error of 0.01 ml. and if there is a drainage error of 0.02 ml. in addition, then the error that is possible in every determination amounts to 0.04 ml. If 40 ml. of standard solution are used, this corresponds to an accuracy of 0.1 per cent. The student therefore should never use a volume of, say, 5 to 10 ml. in a standardization.

4. In general, the titration must be made directly to the end point. A back-titration with another standardized solution increases the possibility of error.

5. In general, the standardization of a solution against another standardized liquid should be avoided, since in every single standardization errors are inherent which may become additive. Thus, sodium hydroxide, for example, should not be standardized with a standardized solution of hydrochloric acid but with a primary standard substance. However, it is desirable to test independently standardized solutions against each other as, for example, 0.1 *N* hydrochloric acid against 0.1 *N* alkali.

6. Every standardization should be based on at least three parallel determinations. The results should agree within 0.1–0.2 per cent.

Any titration, as a rule, involves a titration error (see p. 432), which can be corrected for by the determination of the indicator blank. As a rule, this correction is not applied. If the solution is standardized under the same conditions (amount of reagent used and final volume) as those which obtain in the actual determination, the titration error is practically eliminated. Considered from this point of view, it is preferable to standardize the solution by comparing with a known weight of the substance being determined at the same final volume and under the same experimental conditions.

PROBLEMS

1. Balance the following equations, and derive the equivalent weight (fractions of a mole) of the substance first mentioned:

$H_2C_2O_4 + 2\ NaOH \rightarrow$

$Na_2CO_3 + HCl \rightarrow$

$Na_2CO_3 + 2\ HCl \rightarrow$

$K_2CrO_4 + 2\ AgNO_3 \rightarrow$

$K_2CrO_4 + \cdots KI + \cdots HCl \rightarrow$

$H_3PO_4 + NaOH \rightarrow$

$H_3PO_4 + 2\ NaOH \rightarrow$

$HgCl_2 + 2\ HCN \rightarrow Hg(CN)_2 +$

$2\ AsH_3 + 12\ AgNO_3 + 3\ H_2O \rightarrow As_2O_3 + 12\ HNO_3 + 12\ Ag$

$\cdots K_4Fe(CN)_6 + \cdots KMnO_4 + \cdots H_2SO_4 \rightarrow$

$KCNS + AgNO_3 \rightarrow$

$\cdots HCNS + \cdots 3\ O + H_2O \rightarrow HCN + H_2SO_4$

$3\ Mn^{++} + 2\ MnO_4^- + 2\ H_2O \rightarrow 5\ MnO_2 + 4\ H^+$

$As_2O_3 + 2\ I_2 + 2\ H_2O \rightarrow$

$MnO_2 + 4\ H^+ + 2\ I^- \rightarrow$

$$\left\{\begin{array}{l} HCN + Br_2 \rightarrow BrCN + H^+ + Br^- \\ (BrCN + 2\ I^- \rightarrow I_2 + CN^- + Br^-) \end{array}\right.$$

$VO_4^{\equiv} + Fe^{++} + 6\ H^+ \rightarrow VO^{++} + \cdots$

$\cdots K_2Cr_2O_7 + \cdots KI + \cdots HCl \rightarrow \cdots Cr^{+++} + \cdots.$

2. A solution of hydrochloric acid is standardized with pure sodium carbonate: $Na_2CO_3 + 2\ HCl \rightarrow 2\ NaCl + H_2O + CO_2$. 0.2000 g. of Na_2CO_3 requires 30.00 ml. of the acid. What is the normality of the hydrochloric acid?

Ans. 0.1258 *N*.

3. To 25.00 ml. of 0.1000 *N* $KMnO_4$ an excess of potassium iodide and acid is added. The liberated iodine is titrated with sodium thiosulfate. 26.00 ml. of the latter are required. What is the normality of the thiosulfate?

Ans. 0.0962 *N*.

4. 50.00 ml. of a sulfuric acid solution yield 0.3000 g. of barium sulfate. What is the normality of the acid? *Ans.* 0.0514 *N*.

5. 0.500 g. of impure calcium carbonate is dissolved in 25.00 ml. of 0.5100 *N* hydrochloric acid. The excess of acid (CO_2 does not interfere) is titrated back with 6.50 ml. of 0.4900 *N* NaOH. What is the percentage of calcium carbonate in the sample? *Ans.* 95.75 per cent

6. What should be the normality of a silver nitrate solution in order that each ml. may correspond to 1 mg. of Cl? *Ans.* 0.0282 *N*.

7. How many ml. of 0.2000 *N* silver nitrate are required to precipitate the chloride and the bromide quantitatively in a mixture of 0.2000 g. of KCl and 0.2000 g. of KBr? *Ans.* 21.81 ml.

8. How much water must be added to 1 liter of 0.110 *N* hydrochloric acid to obtain 0.100 *N* acid? *Ans.* 100 ml.

THEORETICAL PART

CHAPTER XXIX

THEORY OF ACIDIMETRY AND ALKALIMETRY

Neutralization analysis.

For a general discussion of the calculation of pH in solutions of acids, bases, salts, and mixtures, the student is referred to Chapter IV (pp. 32–48). Applications of these derivations are made in this chapter.

Acid-base indicators.

The indicators used in acidimetry and alkalimetry are either weak organic acids (indicator acids) or weak organic bases (indicator bases), the dissociated form of which has a color different from that of the undissociated form. If we denote an indicator acid by HI and an indicator base by IOH, then according to the definition the following equilibria exist:

$$\underset{\substack{\textit{(undissociated form}\\ \textit{with acid color)}}}{\mathrm{HI}} \rightleftharpoons \underset{\substack{\textit{(dissociated form}\\ \textit{with alkaline color)}}}{\mathrm{H^+ + I^-}} \tag{1}$$

$$\underset{\substack{\textit{(undissociated form}\\ \textit{with basic color)}}}{\mathrm{IOH}} \rightleftharpoons \underset{\substack{\textit{(dissociated form}\\ \textit{with acid color)}}}{\mathrm{OH^- + I^+}}. \tag{2}$$

Equations (1) and (2) represent the dissociation of weak acids and bases (see discussion in Chapter IV). Application of the mass-action law to (1) gives:

$$\frac{[\mathrm{H^+}][\mathrm{I^-}]}{[\mathrm{HI}]} = K_{\mathrm{I}} \tag{3}$$

in which K_{I} is the *ionization constant* of the indicator; its negative logarithm, $-\log K_{\mathrm{I}} = \mathrm{p}K_{\mathrm{I}}$, is the indicator constant. The color of an indicator acid is determined by the ratio of the concentrations of the two different forms HI and $\mathrm{I^-}$. According to equation (3):

$$\frac{[\mathrm{I^-}]}{[\mathrm{HI}]} = \frac{[\text{Form with alkaline color}]}{[\text{Form with acid color}]} = \frac{K_{\mathrm{I}}}{[\mathrm{H^+}]}. \tag{4}$$

When $[H^+]$ has the same numerical value as K_I, the ratio of $[I^-]$ to $[HI]$ becomes equal to one, meaning that 50 per cent of the indicator is present in the acid form and 50 per cent in the alkaline form. From equation (4) it is seen that at any hydrogen-ion concentration both the forms I^- and HI are present. It should be realized that the human eye has a limited ability to detect either of the two colors when one of the two predominates. If the acid form of the indicator is red, for example, and the alkaline form is yellow and we compare a solution consisting entirely of the red form with one consisting of a mixture of 99 per cent red and 1 per cent yellow, the eye will not be able to detect any difference in color between the two solutions. This will still be the case when the ratio of $[HI]$ to $[I^-]$ is *approximately* equal to 10. In any solution in which the ratio $[I^-] : [HI]$ is smaller than 0.1, we obtain by visual observation the impression that the indicator is present completely in the acid form. Similarly, we get the impression that the indicator is present completely in the alkaline form when the ratio $[I^-]$ to $[HI]$ is greater than 10. (These limits of $\frac{1}{10}$ and 10 are somewhat arbitrary, depending on the color sensitivity of the eye and the particular indicator, but are quite close to the truth.)

From the above then it is clear that we see only the acid color of the indicator when

$$\frac{[I^-]}{[HI]} < 0.1$$

and only the basic color when

$$\frac{[I^-]}{[HI]} > 10.$$

Between the ratios 0.1 and 10 we observe an intermediate color. An indicator, therefore, does not change its color abruptly from that of the acid form to that of the alkaline form at a definite hydrogen-ion concentration but changes gradually over a certain range of $[H^+]$. If we assume that the two limits are determined by the ratio $\frac{[I^-]}{[HI]} > 0.1 < 10$, it is found (equation 4) that

$$\frac{[I^-]}{[HI]} = \frac{1}{10} = \frac{K_I}{[H^+]} \text{ or } [H^+] = 10\,K_I \tag{5}$$

$$\frac{[I^-]}{[HI]} = 10 = \frac{K_I}{[H^+]} \text{ or } [H^+] = \tfrac{1}{10}\,K_I. \tag{6}$$

At $[H^+] = 10\,K_I$ the indicator is present in the acid form, and at $[H^+] = \frac{1}{10}\,K_I$ it is present in the alkaline form. The indicator changes color between

$$[H^+] = \underset{(acid\ color)}{10\,K_I} \quad \text{and} \quad \underset{(alkaline\ color)}{\tfrac{1}{10}\,K_I},$$

or, expressed in pH, between

$$pH = pK_I \pm 1$$

in which pK_I is $-\log K_I$.

This range of pH over which the color change of the indicator takes place is called the *color-change interval* of the indicator. The color-change interval is determined experimentally with the aid of buffer solutions; its exact limits will depend more or less upon the subjective judgment of the observer. In the table below it is indicated that the color-change interval of methyl orange is located between pH 3.1 (red) and 4.4 (yellow-orange). This means then that the pronounced color change takes place between these two pH values. However, another observer might fix these limits, for example, between pH 2.9 and 4.3.

For indicator bases we can derive a relation between color and pH similar to that holding for indicator acids. From equation (2) it is found that

$$\frac{[I^+][OH^-]}{[IOH]} = K_{IOH} \qquad (7)$$

and

$$\frac{[IOH]}{[I^+]} = \frac{\text{Form with alkaline color}}{\text{Form with acid color}} = \frac{[OH^-]}{K_{IOH}} \qquad (8)$$

and since $[OH^-] = \dfrac{K_w}{[H^+]}$

$$\frac{[IOH]}{[I^+]} = \frac{K_w}{K_{IOH}} \cdot \frac{1}{[H^+]} = \frac{K_I}{[H^+]}. \qquad (9)$$

Since $\dfrac{K_w}{K_{IOH}}$ is constant at a given temperature, this quotient can be replaced by K_I, the indicator constant. Expression (9) then becomes similar to (6).

An enormous number of compounds with indicator properties are found in nature and among the products of the laboratory.[1] A selected list of indicators for volumetric purposes (and also for the colorimetric determination of pH) is given in Table LVIII.

---

[1] Compare I. M. Kolthoff, *Acid-Base Indicators*, translated by Ch. Rosenblum, The Macmillan Co., New York, 1937.

TABLE LVIII. COLOR-CHANGE INTERVALS OF SELECTED INDICATORS AT ROOM TEMPERATURE

SCIENTIFIC NAME	TRADE NAME	SOLVENT	NATURE* OF INDICATOR	ACID COLOR	BASIC COLOR	INTERVAL IN pH
Diphenylamino *p*-benzene sodium sulfonate	Tropeoline 00	Water	b	Red	Yellow	1.3– 3.0
Thymolsulfonphthalein	Thymol blue	Water	a	Red	Yellow	1.2– 2.8
Dimethylaminoazobenzene	Methyl yellow	90 per cent alcohol	b	Red	Yellow	2.9– 4.0
Dimethylaminoazobenzene sodium sulfonate	Methyl orange	Water	b	Red	Yellow-orange	3.1– 4.4
Tetrabromphenolsulfonphthalein	Bromphenol blue	Water	a	Yellow	Purple	3.0– 4.6
Tetrabromphenol *m*-cresolsulfonphthalein	Bromcresol green	Water	a	Yellow	Blue	3.8– 5.4
Dimethylaminoazobenzene sodium carbonate	Methyl red (sodium)	Water	b	Red	Yellow	4.2– 6.2
Dichlorosulfonphthalein	Chlorophenol red	Water	a	Yellow	Red	4.8– 6.4
Dibromthymolsulfonphthalein	Bromthymol blue	Water	a	Yellow	Blue	6.0– 7.6
Phenolsulfonphthalein	Phenol red	Water	a	Yellow	Red	6.4– 8.0
Dimethyldiaminophenazin chloride	Neutral red	70 per cent alcohol	b	Red	Yellow-brown	6.8– 8.0
m-Cresolsulfonphthalein	Cresol purple	Water	a	Yellow	Purple	7.4– 9.0
Thymolsulfonphthalein	Thymol blue	Water	a	Yellow	Blue	8.0– 9.6
Phenolphthalein		70 per cent alcohol	a	Colorless	Red-violet	8.0– 9.8
Thymolphthalein		90 per cent alcohol	a	Colorless	Blue	9.3–10.5
p-Nitroaniline azo sodium salicylate	Alizarine yellow	Water	a	Yellow	Violet	10.1–12.0

* a = indicator acid. b = indicator base.

In Figure 78 the color-change intervals of various indicators are represented graphically. It is seen that the above set of indicators covers the pH range between 1 and 12.

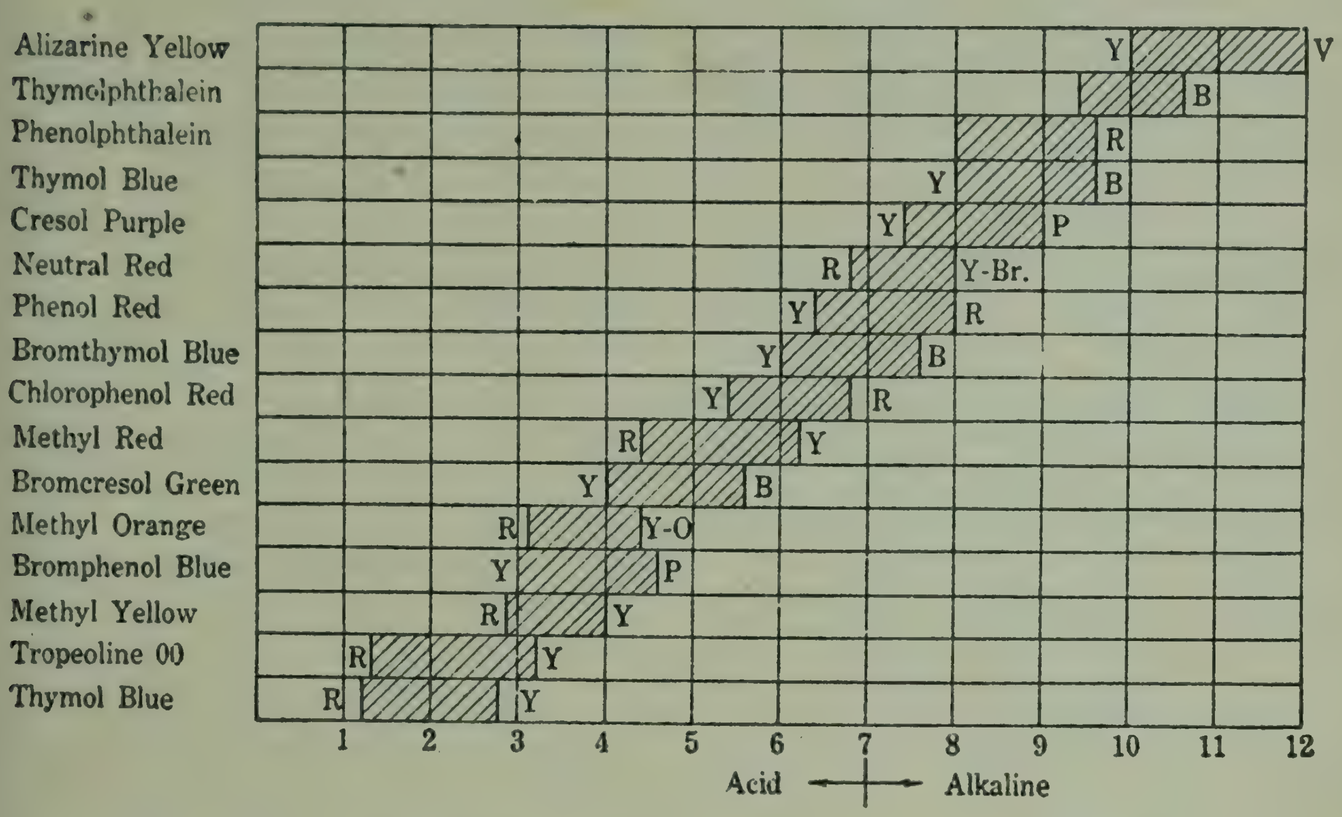


FIG. 78. Color change intervals of some common indicators.

Preparation of indicator solutions.

The stock solutions of the indicators contain 0.5 to 1 g. of indicator per liter of solvent. Tropeoline 00, methyl orange, methyl red sodium salt, and alizarine yellow can be dissolved in water. Methyl yellow, neutral red, phenolphthalein, and thymolphthalein are dissolved in 70 to 90 per cent alcohol.

The sulfonphthaleins are soluble in water if enough sodium hydroxide is added to neutralize the sulfonic group; 100 mg. of these indicators are rubbed in an agate mortar with the specified volume of 0.1 *N* sodium hydroxide solution and then diluted with water to 100 ml. The following volumes of 0.1 *N* sodium hydroxide are required for 100 mg. of the sulfonphthaleins: thymol blue, 2.15 ml.; bromphenol blue, 1.5 ml.; bromcresol green, 1.45 ml.; chlorophenol red, 2.35 ml.; bromthymol blue, 1.6 ml.; phenol red, 2.85 ml.; cresol purple, 2.65 ml.

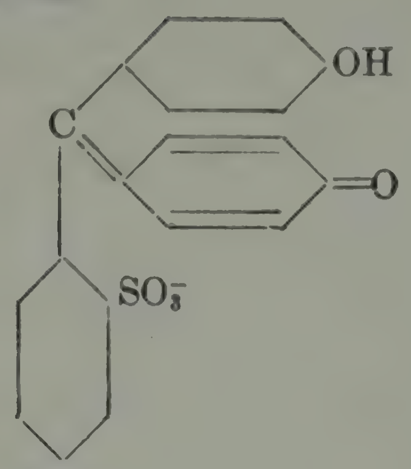
Color change and structural change of indicators.

The color change of an indicator is accompanied by a structural change. On page 450 the structural changes of some of the more representative indicators are given (for further details see the literature).[1]

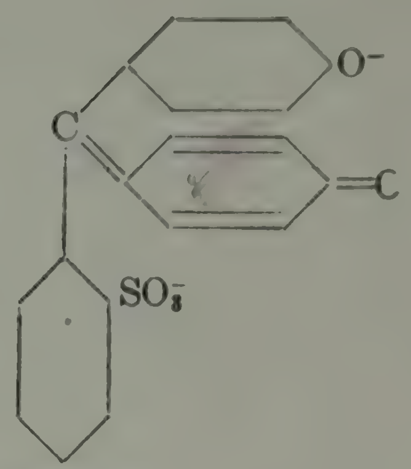
---

[1] Compare I. M. Kolthoff. *Acid-Base Indicators*, translated by Ch. Rosenblum, The Macmillan Co. New York, 1937.

Phenol red:

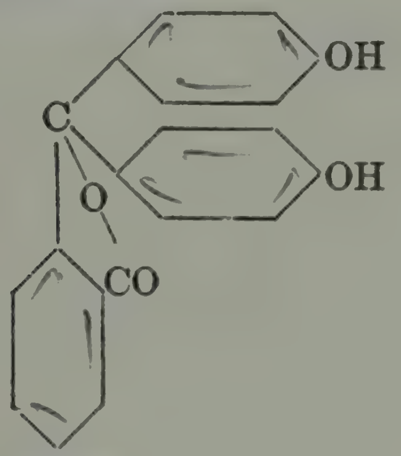


Yellow
(acid form)

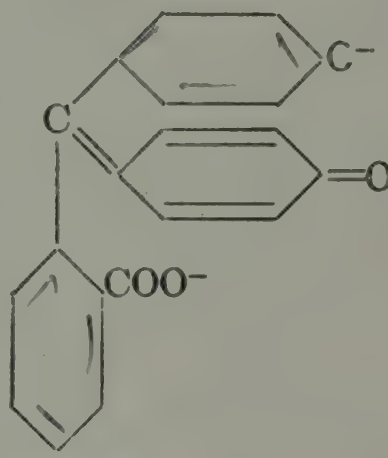


Red
(alkaline form)

Phenolphthalein:

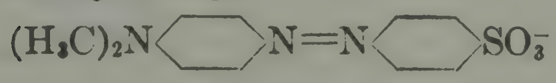


Colorless
(acid form)

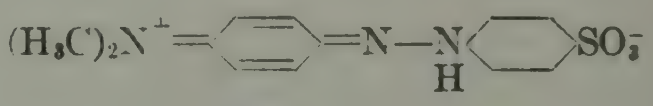


Red-violet
(alkaline form)

Methyl orange:



Yellow-orange
(alkaline form)



Red
(acid form)

Mixed indicators.

In certain cases it is preferable to use a mixture of two indicators or of an indicator and a dye. If a proper selection is made and the indicator and the dye are mixed in the proper ratio, the mixed indicator will give a sharp and pronounced color change at a definite pH and may be used in cases in which the color change is not easily seen with an ordinary indicator. A few of these mixed indicators are given below.[1]

Methyl orange — Indigo carmine: A solution containing 1 g. of methyl orange and 2.5 g. of indigo carmine in 1 liter of water. The alkaline color is green. The mixture exhibits a grayish neutral shade at a pH of 4.0 and changes toward violet in more acid solutions. The stock solution should be kept in brown bottles, best in the dark.

---

[1] For a more complete list see I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis*, Vol. II.

(a) ***Bromcresol green*** (0.1 per cent) — (b) ***Methyl red*** (0.1 per cent): 3 parts of (a) are mixed with 2 parts of (b). Pronounced color change at pH = 5.1; acid color, red; alkaline color, green.

(a) ***Phenolphthalein*** (0.1 per cent) — (b) ***Methylene green*** (0.1 per cent): 1 part of (a) mixed with 2 parts of (b). Color in acid medium, green; at pH = 8.8, pale blue; at pH > 9.0, violet.

(a) ***Cresol red*** (0.1 per cent) — (b) ***Thymol blue*** (0.1 per cent): 1 part of (a) mixed with 3 parts of (b). Acid color, yellow; alkaline color, violet; pink at pH = 8.2; violet at pH = 8.4.

Neutralization of strong acids with strong bases. Neutralization curves.

Since strong acids and bases are completely ionized, it is a simple matter to calculate the change in the hydrogen-ion concentration and the pH during the course of the neutralization of a strong acid with a strong base, or vice versa.

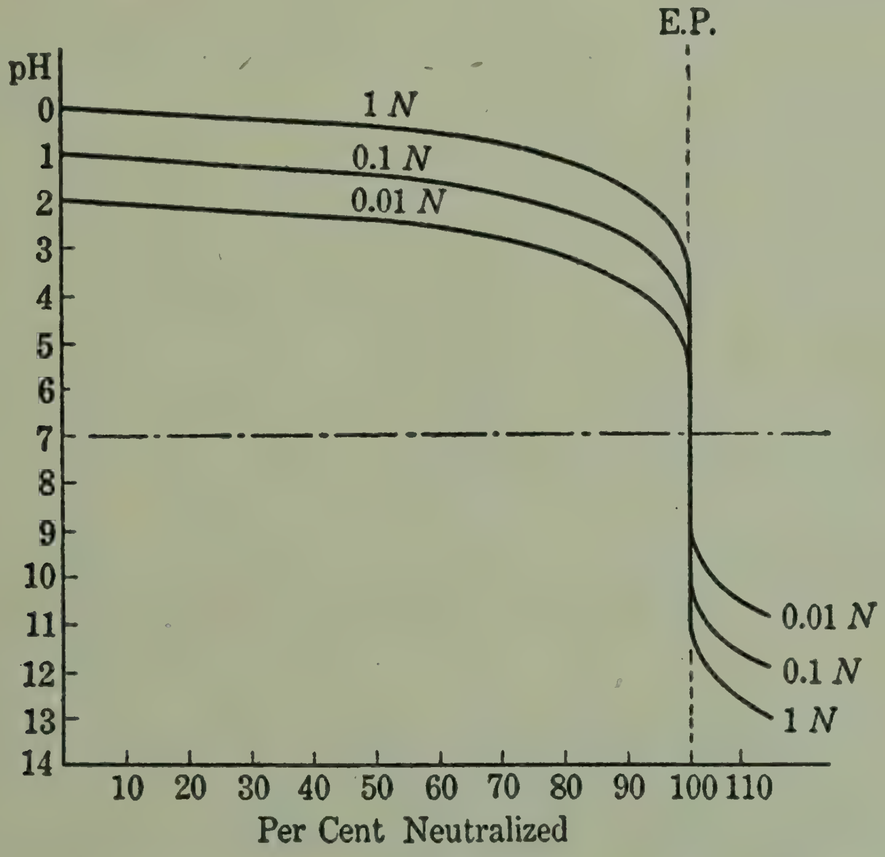


FIG. 79. Neutralization curves of 1 N, 0.1 N, and 0.01 N hydrochloric acid with sodium hydroxide.

If, for example, we start with 100 ml. of 1 N hydrochloric acid and add 90 ml. of 1 N sodium hydroxide solution, there will be 10 ml. of 1 N hydrochloric acid left in a volume of 190 ml. Therefore $[H^+] = \frac{10}{190} \times 1 = 5.3 \times 10^{-2}$, and pH = 1.3. When 100 ml. of 1 N sodium hydroxide have been added, the equivalence point is reached; and the pH should be 7 if no impurities are present. With 101 ml. of 1 N sodium hydroxide there will be 1 ml. of 1 N

sodium hydroxide in excess in a volume of 201 ml.; therefore $[OH^-] = 5 \times 10^{-3}$, $[H^+] = 2 \times 10^{-12}$, and pH = 11.7, etc.

In the following table the change in the pH during the neutralization of 100 ml. of 1 *N*, 0.1 *N*, and 0.01 *N* solutions of a strong acid, respectively, after successive additions of sodium hydroxide of corresponding strength is given. The data are plotted in Figure 79; the curve obtained is called the *neutralization curve*. From the quantitative viewpoint we are especially interested in the changes in the pH near the equivalence point. For this reason, the part of the curve of Figure 79, 2 per cent before and 2 per cent after the equivalence point, is reproduced on an enlarged scale in Figure 80.

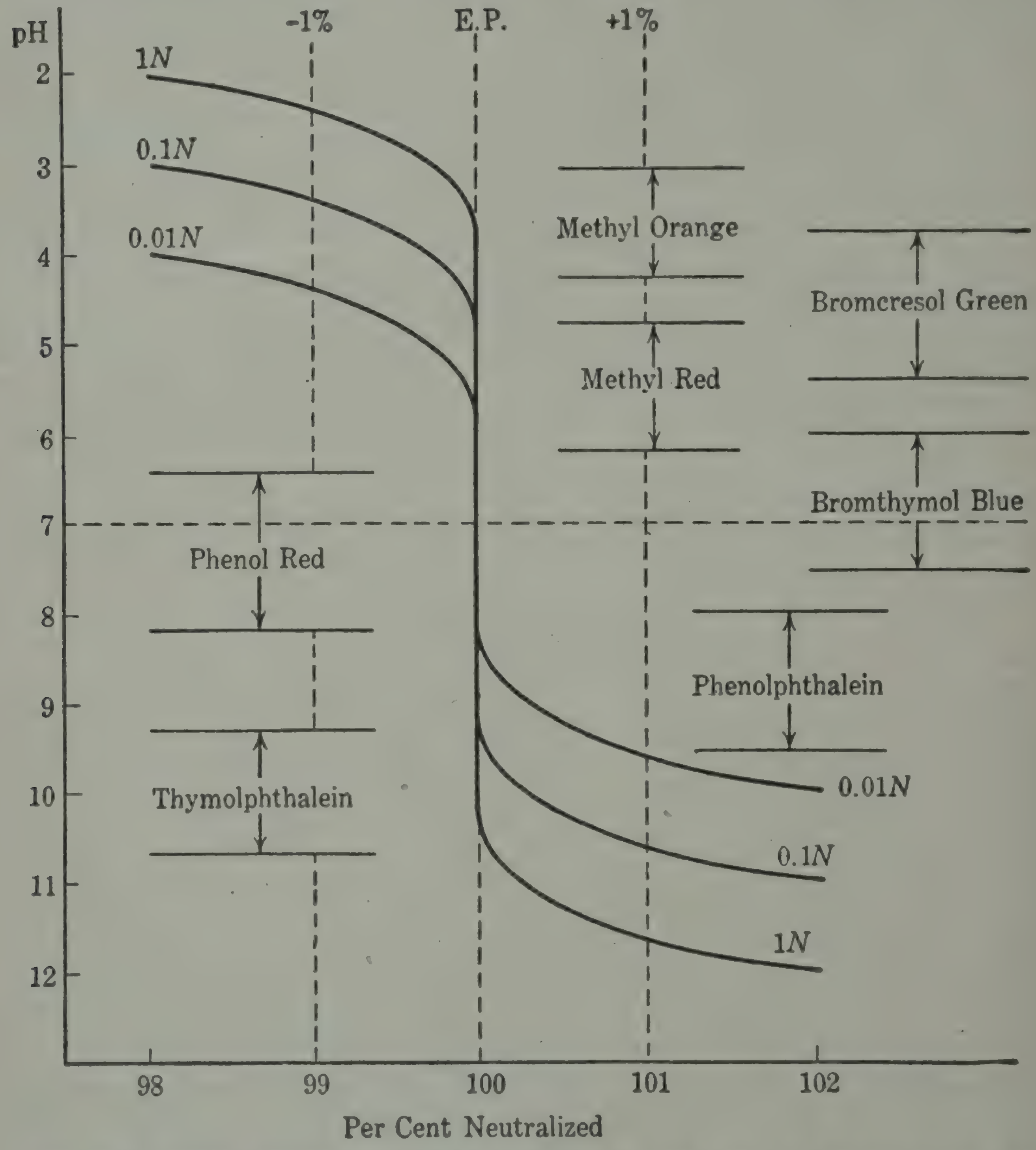


FIG. 80. Neutralization curves of 1 *N*, 0.1 *N*, and 0.01 *N* hydrochloric acid with 1 *N*, 0.1 *N*, and 0.01 *N* sodium hydroxide from 2% before to 2% after the equivalence point.

TABLE LIX. TITRATION OF 100 ML. HCl WITH NaOH AT ROOM TEMPERATURE

NaOH Added in ml. (= % Acid Neutralized)	*N* Solution		0.1 *N* Solution pH	0.01 *N* Solution pH
	[H⁺]	pH		
0	1	0	1.0	2.0
50	3.3×10^{-1}	0.5	1.5	2.5
90	5×10^{-2}	1.3	2.3	3.3
98	1×10^{-2}	2.0	3.0	4.0
99	5×10^{-3}	2.3	3.3	4.3
98.9	1×10^{-3}	3.0	4.0	5.0
99.9	5×10^{-4}	3.3	4.3	5.3
*** E. P. 100.0**	$\mathbf{10^{-7}}$	**7.0**	**7.0**	**7.0**
100.1	2×10^{-11}	10.7	9.7	8.7
100.2	1×10^{-11}	11.0	10.0	9.0
101	2×10^{-12}	11.7	10.7	9.7
102	1×10^{-12}	12.0	11.0	10.0
110	2×10^{-13}	12.7	11.7	10.7

* E. P. = Equivalence point.

The color-change intervals of some of the ordinary indicators are also indicated on this graph. Inspection of Figure 80 or an analysis of the figures in Table LIX reveals: (1) the best titration conditions and (2) the error that is made if an indicator is used which does not change color in the neighborhood of the equivalence point. Let us consider methyl orange (or bromphenol blue) and phenolphthalein (or thymol blue) as indicators covering the most extreme changes of pH.

Methyl orange changes color between pH = 3.0 (red) and 4.2 (yellow-orange), and phenolphthalein between pH = 8.0 (colorless) and 9.8 (violet-red).

Titration of 1 N acid with 1 N sodium hydroxide. After the addition of 99.8 ml. of 1 *N* sodium hydroxide, the pH is 3.0. Methyl orange is then still present in the red form. With 99.9 ml. of sodium hydroxide the pH is 3.3, and therefore most of the indicator is still in the acid form. Upon addition of the last 0.1 ml. of sodium hydroxide, the pH changes abruptly from 3.3 to 7. Therefore a very sharp color change is obtained with methyl orange. If sodium hydroxide is added until the alkaline color just appears, there is no titration error, or, in other words, there is no indicator blank. At the equivalence point phenolphthalein is still present in the acid form; addition of a very small amount of 1 *N* sodium hydroxide will change the pH abruptly to the alkaline side. Thus the addition of 0.1 ml. of 1 *N* base changes the pH from 7 to 10.7; at the latter pH phenolphthalein or thymol blue is present completely in the alkaline form. Summarizing then, it may be said that in the titration of 1 *N* hydrochloric acid with 1 *N* sodium hydroxide any indicator having a color-change interval lying between that of methyl orange and phenolphthalein (and even thymolphthalein) can be used. The indicator blanks are negligibly small, and the color changes are very pronounced.

Titration of 0.1 N hydrochloric acid with 0.1 N sodium hydroxide. With more dilute acids and bases the pH changes near the equivalence point become less abrupt. After the addition of 98 ml. of 0.1 *N* sodium hydroxide to 100 ml. of 0.1 *N* hydrochloric acid, the pH has become equal to 3. On further addition of sodium hydroxide, methyl orange begins to change color from red to the intermediate color. After 99.8 ml. of sodium hydroxide have been added, the pH is 4; and most of the methyl orange is present in the alkaline form. If the titration is stopped here, we are still 0.2 ml. from the equivalence point; the titration error then amounts to 0.2 per cent, and the indicator blank is 0.2 ml. (In this case the indicator blank must be added to the titration figure.) In the titration of 0.1 *N* hydrochloric acid with 0.1 *N* sodium hydroxide, it is advisable to add sodium hydroxide until the indicator is present completely in the alkaline form. For most practical purposes the titration error is then negligibly small. In the reverse titration of 0.1 *N* sodium hydroxide with 0.1 *N* hydrochloric acid with methyl orange as indicator, an excess of acid must be added in order to produce a change from yellow to pink (the first change in color should be considered as the end point). If this color change takes place at a pH of 4.0, the titration error again is 0.2 per cent, and the indicator blank is 0.2 ml. (which in this case is to be subtracted from the amount of acid used). This indicator blank is experimentally determined in the following way:

The solution is titrated in the ordinary manner until the color change of methyl orange to the first pink is noticed. Then in another vessel the same amount of indicator as used in the titration is added to 200 ml. of 0.05 *N* sodium chloride solution, and standard hydrochloric acid is added from a buret until the color of the solution matches that of the titrated solution at the end point.

It is evident that methyl red will give a much sharper color change than methyl orange in the titration of 0.1 *N* solutions. After the addition of 99.9 ml. of 0.1 *N* sodium hydroxide the pH is

4.3, and methyl red is still present in the acid form. Upon the addition of the last 0.1 ml. of sodium hydroxide the pH changes abruptly from 4.3 to 7, and the color of the indicator changes from red to yellow. The titration error is also negligibly small with phenolphthalein as indicator. With 0.1 ml. of 0.1 *N* sodium hydroxide in excess, the pH is 9.7, and most of the phenolphthalein is present in the alkaline form.

The above interpretation is correct only when we work with solutions which do not contain carbon dioxide. Under practical conditions this is never the case, since standard sodium hydroxide as a rule contains a small amount of carbonate. Carbon dioxide is such a weak acid (see p. 461) that it has no effect upon the color of methyl orange; however, it is titrated as a univalent acid with phenolphthalein as indicator. In working with carbon dioxide-free solutions the difference in the amounts of sodium hydroxide used with methyl orange and with phenolphthalein as indicators is not larger than 0.15 to 0.2 ml. of 0.1 *N* sodium hydroxide when 100 ml. of 0.1 *N* hydrochloric acid are titrated. A larger difference will be due to carbon dioxide present in the solution after the end point to methyl orange has been reached.

Titration of 0.01 N hydrochloric acid with 0.01 N sodium hydroxide. It is now a simple matter to specify what indicators should be used in the neutralization of 0.01 *N* hydrochloric acid with 0.01 *N* sodium hydroxide. Methyl orange does not give a sharp color change because the indicator is present in the alkaline form before the equivalence point is reached. After the addition of 90 ml. of 0.01 *N* sodium hydroxide the pH is 3.3; upon further addition of base the color of the indicator changes gradually to yellow-orange. After the addition of 98 to 99 ml. of 0.01 *N* sodium hydroxide, the indicator is practically completely present in the alkaline form. The titration error then amounts to 1 or 2 per cent. In this case it is much better to use methyl red and to titrate to the yellow color. Other indicators which change color between a pH of 5 and 9, such as bromthymol blue, phenol red, or phenolphthalein, can be used as well. Quite generally, when very dilute solutions of a strong acid must be titrated with a strong base (or vice versa), it is preferable to carry out the titration at boiling temperature, using phenolphthalein, phenol red, bromthymol blue, or methyl red as indicator. Any carbon dioxide present is expelled by boiling the slightly acid solution. The latter should be cooled before the final color adjustment.

Neutralization of weak acids with strong bases or weak bases with strong acids.

In the following discussion the titration of 0.1 *N* solutions of weak acids with strong bases or of 0.1 *N* solutions of weak bases with strong acids only will be considered. It is a simple matter to make similar derivations for other concentrations. Whereas in the titration of 0.1 *N* solutions of a strong acid with a strong base we can select any indicator changing color between a pH of 4 and 10, we are much more limited as regards choice of indicator in the titration of weak acids (with strong bases) or of weak bases (with strong acids).

This is evident from a study of the neutralization curves. In Chapter IV equations for the calculation of the pH of a solution of a weak acid (p. 35), of mixtures of the weak acid and its salt (p. 43), and of solutions of the salt of the acid with a strong base (p. 40) were derived. These equations are used in the calculation of the neutralization curves.

In the following table the neutralization curves of 0.1 *N* acetic acid ($K_a = 1.8 \times 10^{-5}$), and of a weaker acid with an ionization constant of 10^{-7} with 0.1 *N* sodium hydroxide are given.

TABLE LX. NEUTRALIZATION CURVES OF 100 ML. 0.1 *N* ACETIC ACID ($K_a = 1.8 \times 10^{-5}$) AND OF 100 ML. 0.1 *N* HA ($K_a = 10^{-7}$) WITH 0.1 *N* SODIUM HYDROXIDE AT ROOM TEMPERATURE ($K_w = 10^{-14}$)

0.1 *N* NaOH ADDED IN ML. (= % ACID NEUTRALIZED)	0.1 *N* ACETIC ACID pH	0.1 *N* ACID $K_a = 10^{-7}$ pH
0	2.87	4.0
10	3.80	6.0
50	4.75	7.0
90	5.70	8.0
99.0	6.75	9.0
99.8	7.45	9.62
99.9	7.75	9.78
E. P. **100.0**	**8.72**	**9.85**
100.1	9.7	10.00
100.2	10.0	10.19
101	10.7	10.7

These data are plotted in Figure 81; for comparison the neutralization curve of 0.1 *N* hydrochloric acid is added. In addition, the color-change intervals of methyl orange (M.O.), methyl red (M.R.), and phenolphthalein (Phpht.) are indicated.

An inspection of the neutralization curve of acetic acid shows that methyl orange cannot be used as indicator. It changes from red to yellow-orange between a pH of 3.0 and 4.2. At the latter pH only 30 per cent of the acid is neutralized, and the titration error would amount to 70 per cent. Methyl red is not a good indicator either because it begins to change color at a pH of about 4.6, i.e., before 50 per cent of the acid has been neutralized, and is present in the yellow form at a pH of 6.0 when about 93 per cent of the acid has been neutralized. In order to get a good result it is necessary to use an indicator which changes color in the neighborhood of the pH prevailing at the equivalence point. Since the solution has a slightly alkaline reaction at the equivalence point, an indicator changing color in alkaline medium must be used. It is evident that phenolphthalein and thymol blue are the best indicators. *Quite generally weak acids should be titrated with phenolphthalein, thymol blue, or thymolphthalein as indicators.*

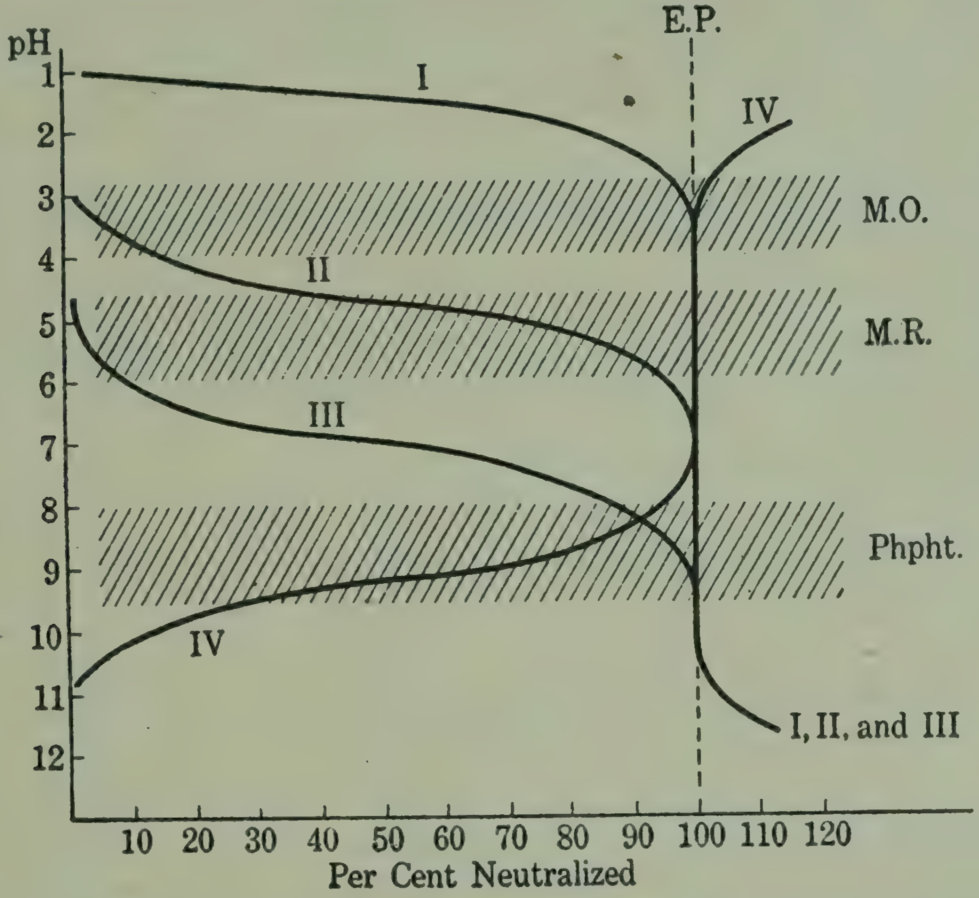


FIG. 81. Neutralization curves of 0.1 N acid and of 0.1 N ammonia (I) 0.1 N HCl (II) 0.1 N acetic acid, $K_a = 1.8 \times 10^{-5}$ (III) 0.1 N HA, $K_a = 10^{-7}$ (IV) 0.1 N NH_3, $K_b = 1.8 \times 10^{-5}$.

The changes in pH near the equivalence point become less pronounced with a decrease in the ionization constant of the acid, because hydrolysis then begins to play a more important rôle. In the titration of 0.1 N solutions of acids having an ionization constant of the order of 10^{-7}, it is seen from the table that even thymol blue and phenolphthalein do not yield good end points. After 90 per cent of the acid has been neutralized, the pH = 8.0; and upon further addition of sodium hydroxide the two indicators will only gradually change their colors to the alkaline side, and no sharp end point is obtained. Thymolphthalein is still useful in this case, since it begins to change color at a pH of about 9.6, 0.2 per cent before the end point. Acids having an ionization constant smaller than 10^{-7} cannot be satisfactorily titrated in 0.1 *N* solutions.

In the following table the neutralization curve of 0.1 *N* ammonium hydroxide with 0.1 *N* hydrochloric acid is given (see also Fig. 81).

TABLE LXI. NEUTRALIZATION CURVE OF 100 ML. 0.1 *N* AMMONIUM HYDROXIDE ($K_b = 1.8 \times 10^{-5}$) WITH 0.1 *N* HYDROCHLORIC ACID AT ROOM TEMPERATURE ($K_w = 10^{-14}$)

0.1 *N* HCl ADDED IN ML. (= % BASE NEUTRALIZED)	pH
0	11.13
10	10.20
50	9.25
90	8.30
99.0	7.25
99.8	6.55
99.9	6.25
E. P. **100.0**	**5.25**
100.1	4.3
100.2	4.0
101.0	3.3

From the data it is evident that none of the indicators changing color in alkaline medium will yield a good end point. Phenolphthalein gives a very gradual color change and becomes colorless when about 94 per cent of the ammonia has been neutralized. Methyl red, methyl orange, and other indicators changing color at pH values between approximately 6 and 3 should be used. *Quite generally weak bases are titrated with methyl red, chlorphenol red, bromcresol green, bromphenol blue, or methyl orange as indicators.*

In the titration of weak acids with weak bases (e.g., acetic acid with ammonia), the pH changes near the equivalence point are always very gradual, and no sharp end point can be found with any indicator. Useful results can be obtained by using an indicator which assumes an intermediate color at the end point and employing buffer solutions with the same pH as the solution at the equivalence point, with the same amount of indicator, for comparison.[1] If possible, however, one should always titrate a weak acid with a strong base, and a weak base with a strong acid.

Polybasic acids.

Acids containing more than one replaceable hydrogen are polybasic acids (dibasic, tribasic, etc.). In many of these acids all the replaceable hydrogen can be titrated. This, for example, is the case with sulfuric acid (a strong acid), oxalic, tartaric, succinic, citric, phthalic, malonic, and maleic acids (weak acids).

If the difference between the first and second ionization constants of a dibasic acid is very great ($K_1 : K_2 = 10{,}000$), it is possible to titrate the acid as a uni- and as a divalent acid separately. This, for example, is the case with phosphoric acid and sulfurous acid. Carbonic acid is determined only as a monobasic acid by direct titration.

Phosphoric acid.

$$H_3PO_4 \rightleftarrows H^+ + H_2PO_4^- \qquad \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = K_1 = 7 \times 10^{-3}$$

$$H_2PO_4^- \rightleftarrows H^+ + HPO_4^= \qquad \frac{[H^+][HPO_4^=]}{[H_2PO_4^-]} = K_2 = 7 \times 10^{-8}$$

$$HPO_4^= \rightleftarrows H^+ + PO_4^{\equiv} \qquad \frac{[H^+][PO_4^{\equiv}]}{[HPO_4^=]} = K_3 = 5 \times 10^{-13}.$$

In mixtures of phosphoric acid with monosodium phosphate, NaH_2PO_4, the pH can be calculated as in any other buffer solution:

$$[H^+] = \frac{[H_3PO_4]}{[H_2PO_4^-]} K_1.$$

In mixtures of mono- and disodium phosphate the pH is calculated in a similar way from K_2:

$$[H^+] = \frac{[H_2PO_4^-]}{[HPO_4^=]} K_2.$$

In the titration of phosphoric acid as a univalent acid, sodium hydroxide is added until all of the acid has been transformed into NaH_2PO_4; an indicator should be used which changes color at the pH of a NaH_2PO_4 solution.

---

[1] For further details see I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis*, Vol. I (1942), Vol. II (1943), Interscience Publishers, Inc., New York.

The pH of the latter can be calculated from the two ionization constants (see Chapter IV, p. 37).

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^=. \qquad (1)$$

In this case $[H^+]$ is not equal to $[HPO_4^=]$, since part of the hydrogen ions combine with $H_2PO_4^-$ to form H_3PO_4:

$$H^+ + H_2PO_4^- \rightleftharpoons H_3PO_4. \qquad (2)$$

Therefore the sum of the concentrations of H^+ and H_3PO_4 is equal to $[HPO_4^=]$:

$$[H^+] + [H_3PO_4] = [HPO_4^=]. \qquad (3)$$

We know that

$$\frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = K_1 \qquad (4)$$

$$\frac{[H^+][HPO_4^=]}{[H_2PO_4^-]} = K_2 \qquad (5)$$

From (3) and (5)

$$[HPO_4^=] = [H^+] + [H_3PO_4] = \frac{[H_2PO_4^-]}{[H^+]} K_2. \qquad (6)$$

From (4) $$[H_3PO_4] = \frac{[H^+][H_2PO_4^-]}{K_1} \qquad (7)$$

$$[H^+] = \frac{[H_2PO_4^-]}{[H^+]} K_2 - \frac{[H^+][H_2PO_4^-]}{K_1} \text{ [eq. (6) – eq. (7)]} \qquad (8)$$

or $$[H^+]^2 = \frac{K_1K_2[H_2PO_4^-]}{K_1 + [H_2PO_4^-]}. \qquad (9)$$

Since NaH_2PO_4 is a strong electrolyte, $[H_2PO_4^-]$ can be put equal to the molar concentration c:

$$[H^+] = \sqrt{\frac{K_1K_2c}{K_1 + c}}. \qquad (10)$$

If K_1 is small compared with c, $K_1 + c$ becomes virtually equal to c; and instead of (10) we may write the approximate equation

$$[H^+] = \sqrt{K_1K_2}, \qquad (11)$$

and $$pH = \tfrac{1}{2}(pK_1 + pK_2). \qquad (12)$$

In the case of phosphoric acid, $K_1 = 7 \times 10^{-3}(pK_1 = 2.16)$, $K_2 = 7 \times 10^{-8}$ $(pK_2 = 7.16)$; therefore a solution of NaH_2PO_4 has a pH of

$$\tfrac{1}{2}(2.16 + 7.16) = 4.66.$$

Phosphoric acid can be titrated as a monobasic acid (1 equivalent = 1 mole), using methyl orange or bromcresol green as indicators. It is advisable in this case to use an equal volume of NaH_2PO_4 solution containing the same amount of indicator as the unknown for comparison at the end point.

The pH of a solution of Na_2HPO_4 can be calculated from K_2 and K_3. $K_3 = 5 \times 10^{-13}$; $pK_3 = 12.3$.

$$pH = \tfrac{1}{2}(7.16 + 12.3) = 9.7.$$

At this pH phenolphthalein and thymol blue are already present in the alkaline form, and they will give a color change before the end point is reached. Thymolphthalein, however, is a suitable indicator, since it begins to change color at a pH of 9.6.[1]

The third ionization constant of phosphoric acid is extremely small; a solution of Na_3PO_4 is strongly hydrolyzed, and the acid cannot be determined as a tribasic acid by direct titration. If the trivalent phosphate ions are removed by precipitation, they cannot hydrolyze; and under these conditions it is possible to determine phosphoric acid as a tribasic acid. This is done by the addition of a large excess of calcium chloride:

$$2\ Na_2HPO_4 + 3\ CaCl_2 \rightarrow Ca_3(PO_4)_2 + 4\ NaCl + 2\ HCl.$$

Carbonic acid. The ionization constants of carbonic acid are:

$$K_1 = 3 \times 10^{-7}(pK_1 = 6.5) \text{ and } K_2 = 6 \times 10^{-11}(pK_2 = 10.2).$$

A solution of sodium bicarbonate therefore has a pH given by the expression:

$$pH = \tfrac{1}{2}(6.5 + 10.2) = 8.35.$$

Carbon dioxide can be titrated as a monobasic acid, using phenolphthalein or thymol blue (or a mixed indicator, see p. 450 and p. 558) as indicator. The color change is not sharp, and it is necessary to use a solution of freshly prepared pure sodium bicarbonate with the same amount of indicator for comparison.

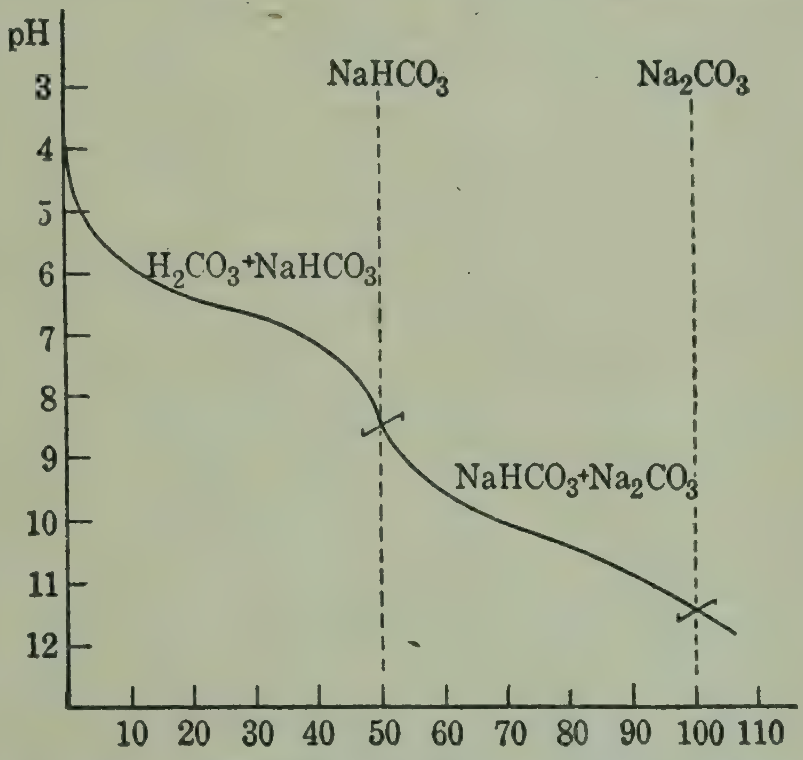


FIG. 82. Titration of 100 ml. 0.05 *M* H_2CO_3 with 0.1 *N* sodium hydroxide.

The second ionization constant of carbonic acid is so small that it cannot be determined as a dibasic acid by a direct titration. However, the carbonate ion can be removed by precipitation. A measured excess of barium hydroxide is added to the solution of carbon dioxide or bicarbonate:

$$H_2CO_3 + Ba(OH)_2 \rightarrow BaCO_3 + 2\ H_2O$$
$$2\ NaHCO_3 + 2\ Ba(OH)_2 \rightarrow 2\ BaCO_3 + 2\ NaOH + 2\ H_2O,$$

and the excess is titrated back with standard acid, using phenolphthalein or thymol blue as indicator, without filtering off the barium carbonate.

In the following table, data for the neutralization curve of carbon dioxide to $NaHCO_3$ and Na_2CO_3 are given (see also Fig. 82).

---

[1] For the determination of ortho-, meta-, and pyrophosphoric acids in a mixture, see A. B. Gerber and F. T. Miles, Ind. Eng. Chem., Anal. Ed. *10*, 519 (1938).

TABLE LXII. DATA FOR NEUTRALIZATION CURVE OF CARBON DIOXIDE

100 ml. of 0.05 *M* carbon dioxide titrated with 0.1 *N* NaOH
$K_1 = 3 \times 10^{-7}$; $K_2 = 6 \times 10^{-11}$

0.1 *N* NaOH ADDED	pH
ml.	
0	3.9
0.5	4.5
5	5.5
25	6.5
45	7.5
49	7.95
49.5	8.15
50 $NaHCO_3$	**8.35** (Phpht.; thymol blue)
50.5	8.7
51	8.8
55	9.2
75	10.2
95	11.2
100 Na_2CO_3	**11.4** (No good indicator here)
105	11.75

Replacement titrations. Titration of the base in a salt of a weak acid, and titration of the acid in a salt of a weak base.

A salt of a weak acid, HA, may be considered to be a strong electrolyte. Therefore the salt, NaA, is completely ionized in aqueous medium into Na^+ and A^-. The A ions are derived from a weak acid and react with the hydrogen ions of a strong acid added to form undissociated acid:

$$A^- + H^+ \rightleftarrows HA.$$

The equivalence point is reached when an amount of standard acid equivalent to the amount of base in the salt has been added. If the acid is very weak, the pH at the end point may be of the order of 4 to 5; further addition of standard acid results in a fairly abrupt decrease of the pH. Thus it is possible to determine the end point with an indicator which changes color at a pH close to that of the solution at the equivalence point. The titration curve in such a titration, in which the anion of the weak acid is replaced by that of a strong acid, is the reciprocal of the neutralization curve and can be constructed in exactly the same way. Potassium cyanide, for example, is a salt of the weak acid HCN ($K_a = 10^{-9}$). If a 0.2 *N* solution of the salt is titrated with 0.2 *N* hydrochloric acid, the solution at the equivalence point contains

0.1 equivalent of HCN per liter. Therefore the pH of the solution is $-\log 10^{-5} = 5$. If an excess of acid corresponding to 0.1 per cent is added, the pH decreases to 4, and with 1 per cent excess of acid to 3. Therefore methyl red, methyl orange, bromcresol green, and bromphenol blue will be suitable indicators in the titration of potassium cyanide with acid. The same considerations hold in the titration of borax. This salt in solution may be considered as boric acid which is half neutralized:

$$Na_2B_4O_7 \rightarrow 2\ Na^+ + B_4O_7^=$$
$$B_4O_7^= + 5\ H_2O \rightarrow 2\ H_3BO_3 + 2\ H_2BO_3^-$$
$$2\ H_2BO_3^- + 2\ H^+ \rightarrow 2\ H_3BO_3$$

or summarized:

$$Na_2B_4O_7 + 2\ HCl + 5\ H_2O \rightarrow 2\ NaCl + 4\ H_3BO_3.$$

Sodium carbonate can be titrated in two ways:

(a) $$CO_3^= + H^+ \rightarrow HCO_3^-.$$

The pH of a sodium bicarbonate solution is 8.35; therefore phenolphthalein or thymol blue or a mixed indicator must be used The color change is not sharp, and it is best to use a solution of pure sodium bicarbonate for comparison (see Table LXII on p. 462 and Fig. 82 on p. 461).

Sodium carbonate can also be titrated with two equivalents of acid:

(b) $$CO_3^= + 2\ H^+ \rightarrow H_2CO_3.$$

In the same way $NaHCO_3$ can be titrated to H_2CO_3:

$$NaHCO_3 + HCl \rightarrow NaCl + H_2CO_3.$$

An inspection of the neutralization curve of carbonic acid (see Table LXII and Fig. 82) shows that methyl red cannot be used as indicator, since it exists completely in the acid form before the equivalence point is reached. Methyl orange, bromphenol blue, and bromcresol green are suitable indicators. If the carbon dioxide formed in the titration is removed by boiling, any of the other indicators may be used as well. The method is also applied to the volumetric determination of calcium carbonate. This is dissolved in a known excess of standard acid and the latter back-titrated, after boiling off the carbon dioxide, with standard base, any of the indicators which are applied in the neutralization of a strong acid with a strong base being used.

Salts of very weak bases can be titrated with a strong base. Aniline hydrochloride is a salt of the weak base aniline ($K_b = 10^{-9}$).

In the titration of a 0.2 *M* solution of the salt with 0.2 *N* NaOH, the pH at the end point is 9; and phenolphthalein and thymol blue are suitable indicators.

Theoretically, salts of the heavy metals, whose hydroxides are fairly weak and in addition very slightly soluble, can be titrated in a similar way:

$$Al^{+++} + 3\,Cl^- + 3\,OH^- \rightarrow Al(OH)_3 + 3\,Cl^-.$$

However, difficulties arise from the formation of slightly soluble basic salts. Satisfactory results are usually obtained by the addition of an excess of base and back-titration of the latter. The method can even be applied to the determination of magnesium in its salts. Although magnesium hydroxide is a strong base, it is slightly soluble (solubility product $= 10^{-11}$). An excess of standard base is added to the magnesium salt solution, and the excess base in the *clear* supernatant liquid or in the filtrate is back-titrated with standard acid.

Hydrolytic precipitation and complex formation reactions.

If a solution of potassium cyanide is added to water, the latter will become alkaline as a result of the hydrolysis:

$$CN^- + H_2O \rightleftarrows OH^- + HCN.$$

If cyanide ions are removed by the formation of a slightly soluble or slightly dissociated compound, the solution will not become alkaline until cyanide is in excess. Mercuric cyanide is a substance which is much less dissociated than mercuric chloride. Therefore the following reaction runs quantitatively to the right:

$$HgCl_2 + 2\,CN^- \rightarrow Hg(CN)_2 + 2\,Cl^-.$$

The mercuric chloride solution will have an acid reaction towards methyl red. When all the mercuric chloride has been transformed into cyanide, the color changes very sharply from red to yellow. In such a titration the mercuric chloride should not contain free acid, and the reagent should be free from acidic and basic impurities.

A solution of an alkali cyanide can be titrated with standard silver nitrate, using an acid-base indicator such as phenolphthalein or phenol red for the detection of the end point. The cyanide is transformed into the complex $Ag(CN)_2^-$ ion:

$$2\,CN^- + Ag^+ \rightarrow Ag(CN)_2^-,$$

which is the anion of a strong acid. The solution of its alkali salt accordingly has a neutral reaction. Therefore, after the removal of the last trace of cyanide with silver ions, the reaction changes from alkaline to neutral.

An important application of a hydrolytic precipitation reaction is made in the determination of the hardness of water (sum of calcium and magnesium). Potassium palmitate solutions (soap) are strongly hydrolyzed and have an alkaline reaction. Such a solution gives insoluble palmitates with calcium, magnesium, barium, strontium, and some other cations:

$$2\ \mathrm{K\ Palm} + \mathrm{Ca}^{++} \rightarrow \mathrm{Ca(Palm)_2} + 2\ \mathrm{K}^{+}.$$

For the determination of the sum of calcium and magnesium in water, the latter is neutralized with acid to methyl orange (titration of the bicarbonate). After boiling off the carbon dioxide, the solution will have a neutral reaction after cooling. It is then titrated with the soap solution, using phenolphthalein as indicator.

One might expect that sodium carbonate would be a useful reagent in the determination of the alkaline earths. The carbonates of calcium, strontium, and barium are very slightly soluble; and their saturated solutions have a pH of about 9. If an excess of the alkaline earth ion is present, the pH is less than 9; and with an excess of sodium carbonate, it is greater. Actually the precipitation of the alkaline earth carbonates during titration with sodium carbonate is rather slow; the direct titration, therefore, is not very useful. Addition of an excess of the standard carbonate solution and back-titration of the filtrate, however, yield good results.

Various other reagents are used in hydrolytic precipitation and complex formation reactions:[1]

Potassium chromate for barium: $\mathrm{CrO_4^{=}} + \mathrm{Ba^{++}} \rightleftarrows \mathrm{BaCrO_4}$
$\mathrm{CrO_4^{=}} + \mathrm{H_2O} \rightleftarrows \mathrm{HCrO_4^{-}} + \mathrm{OH^{-}}$.

Aluminum chloride for fluoride: $\mathrm{Al^{+++}} + 6\ \mathrm{F^{-}} \rightleftarrows \mathrm{AlF_6^{\equiv}}$
$\mathrm{Al^{+++}} + \mathrm{H_2O} \rightleftarrows \mathrm{Al(OH)^{++}} + \mathrm{H^{+}}$.

Mercuric perchlorate for halides: $\mathrm{Hg^{++}} + 2\ \mathrm{Cl^{-}} \rightarrow \mathrm{HgCl_2}$
$\mathrm{Hg^{++}} + \mathrm{H_2O} \rightleftarrows \mathrm{Hg(OH)^{+}} + \mathrm{H^{+}}$.

Sodium sulfide for zinc: $\mathrm{Zn^{++}} + \mathrm{S^{=}} \rightarrow \mathrm{ZnS}$
$\mathrm{S^{=}} + \mathrm{H_2O} \rightarrow \mathrm{HS^{-}} + \mathrm{OH^{-}}$.

PROBLEMS

1. Derive the neutralization curve of 0.2 N hydrochloric acid with 0.2 N sodium hydroxide at room temperature. What is the titration error when methyl orange is used as indicator (pH at end point = 4.0), methyl red (pH at end point = 6.0), phenolphthalein (pH at end point = 9.0), and thymolphthalein (pH at end point = 10.0)?

2. Derive the neutralization curve of 0.1 N formic acid with 0.1 N sodium hydroxide at room temperature. What is the titration error with methyl red (pH at end point, 6.0), phenol red (pH at end point = 8.0), and phenolphthalein (pH at end point = 9)? $K_a = 10^{-4}$; $K_w = 10^{-14}$.

3. Derive the neutralization curve of 1 N ammonium hydroxide with 1 N hydrochloric acid at room temperature. What is the titration error with methyl orange (pH at end point = 4.0), methyl red (pH at end point = 5.0), phenol red (pH at end point = 7.0), and phenolphthalein (pH at end point = 8)? $K_{NH_3} = 1.8 \times 10^{-5}$; $K_w = 10^{-14}$.

---

[1] For details see I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis*, Vol. II (1943).

4. Sulfurous acid is a dibasic acid. $K_1 = 1 \times 10^{-2}$; $K_2 = 1.0 \times 10^{-7}$. Can it be titrated as a monobasic acid? What is the pH of a solution of $NaHSO_3$? What indicators could be used? Can it be titrated as a dibasic acid? What is the pH of a 0.1 molar solution of Na_2SO_3? ($K_w = 10^{-14}$.) What indicator should be used?

5. 0.1 *N* borax solution is to be titrated with 0.1 *N* hydrochloric acid. What will be the pH at the end point? What indicator should be used? $K_a = 10^{-9}$.

6. 25.00 ml. of 0.2514 *N* sodium hydroxide solution are added to 50.00 ml. of 0.1012 *N* magnesium sulfate solution, and the mixture diluted to 100 ml. in a volumetric flask. 50.00 ml. of the filtrate are back-titrated with 0.1046 *N* hydrochloric acid. How much acid will be required? What indicator should be used? How much magnesium remains in solution after the addition of the sodium hydroxide? $[Mg^{++}][OH^-]^2 = 10^{-11}$.

Ans. 5.85 ml. acid; $[Mg^{++}] = 6.9 \times 10^{-8}$ molar.

7. A solution is 0.1 *N* in hydrochloric acid and 0.2 *N* (*M*) in boric acid. To 50 ml. of this solution are added 50 ml. of 0.1 *N* sodium hydroxide. What is the pH of the mixture after addition of the sodium hydroxide? ($K_{H_3BO_3} = 5 \times 10^{-10}$.) What indicator should be used in the titration of hydrochloric acid in the presence of boric acid?

Ans. pH = 5.15.

8. A solution of 0.1 *N* hydrochloric acid is titrated with 0.1 *N* sodium hydroxide. The pH at the end point is 4.0. Calculate the titration error.

Ans. − 0.2 per cent.

9. Pure water exposed to carbon dioxide was found to have a pH of 4.52. (a) Calculate the carbon dioxide concentration of the water ($K_{1H_2CO_3} = 3 \times 10^{-7}$). (b) How much 0.01 *N* barium hydroxide is necessary to precipitate all of the carbon dioxide in 100 ml. of the water?

Ans. (a) 3×10^{-3} *M*.

CHAPTER XXX

THEORY OF PRECIPITATION AND COMPLEX-FORMATION ANALYSIS

Precipitation analysis. Argentimetry.

The most important volumetric precipitation reactions are carried out with silver nitrate as the reagent. These methods, involving the use of a standard solution of silver nitrate, are called argentimetric methods and will be discussed in detail in this chapter. The general principles, however, also hold for any other precipitation method.

Titration curves.

The change in the silver-ion concentration and that of the anion precipitated during the course of a titration can be calculated from the solubility product of the silver salt formed, and the concentrations of the solution titrated and the silver nitrate solution. Let us assume that 50 ml. of 0.2 *N* sodium chloride are titrated with 0.2 *N* silver nitrate. After the addition of 40 ml. of 0.2 *N* silver solution, there are left 10 ml. of 0.2 *N* sodium chloride in a volume of 90 ml. (compare p. 451). Therefore $[\mathrm{Cl^-}] = \frac{10}{90} \times 0.2 = 0.022$, and $\mathrm{pCl^-} = 1.66$. Since the solubility product of silver chloride is 10^{-10}, we have

$$[\mathrm{Ag^+}][\mathrm{Cl^-}] = 10^{-10} = S,$$

or

$$\mathrm{pAg^+} + \mathrm{pCl^-} = 10 = \mathrm{p}S,$$

and in this particular case

$$\mathrm{pAg^+} = 10 - 1.66 = 8.34.$$

After the addition of 50 ml. of 0.2 *N* silver nitrate, the equivalence point is reached; and a saturated solution of silver chloride with no excess of chloride or silver is obtained. At this point

$$[\mathrm{Ag^+}] = [\mathrm{Cl^-}] = \sqrt{S} = \sqrt{10^{-10}}$$
$$\mathrm{pAg^+} = \mathrm{pCl^-} = \tfrac{1}{2}\log S = 5$$

With 0.05 ml. of silver nitrate in excess, $[Ag^+] = 10^{-4}$; hence

$$pAg^+ = 4 \text{ and } pCl^- = 6.$$

Quite near the equivalence point, the values of $[Ag^+]$ or $[Cl^-]$ are larger than correspond to the excess of either ion added to the solution, since the dissolved silver chloride contributes some silver and chloride ions to the solution. If the excess of Ag^+ corresponds to the concentration A and the solubility of silver chloride in this excess is x, then:

$$[Cl^-] = x, \text{ and } [Ag^+] = A + x, \text{ and } x(A + x) = S_{AgCl} = 10^{-10}.$$

If A is greater than approximately $10\sqrt{S}$, $(A + x)$ becomes virtually equal to A, and the simple calculation applied above may be used.

In the following table, values of pCl^- and pAg^+ for the titration of 100 ml. of 0.1 N sodium chloride with 0.1 N silver nitrate are given (solubility product of silver chloride $= 10^{-10}$). In addition the corresponding figures for pI^- and pAg^+ are given for the titration of 100 ml. of 0.1 N alkali iodide with 0.1 N silver nitrate.

TABLE LXIII. TITRATION OF 100 ML. 0.1 N NaCl AND 100 ML. 0.1 N KI RESPECTIVELY WITH 0.1 N $AgNO_3$ ($S_{AgCl} = 10^{-10}$; $S_{AgI} = 10^{-16}$)

0.1 N $AgNO_3$ ADDED IN ML. (HALIDE PPTD. IN %)	TITRATION OF CHLORIDE		TITRATION OF IODIDE	
	pCl^-	pAg^+	pI^-	pAg^+
0	1	....	1	...
90	2.3	7.7	2.3	13.7
98	3.0	7.0	3.0	13.0
99	3.3	6.7	3.3	12.7
99.8	4.0	6.0	4.0	12.0
99.9	4.3	5.7	4.3	11.7
E. P. **100**	**5.0**	**6.0**	**8.0**	**8.0**
100.1	5.7	4.3	11.7	4.3
100.2	6.0	4.0	12.0	4.0
101	6.7	3.3	12.7	3.3
110	7.7	2.3	11.7	2.3

In Figure 83 are represented the changes of pAg^+ in the region between 10 per cent before and 10 per cent after the equivalence point in the titration of 0.1 N chloride and 0.1 N iodide, respectively, with 0.1 N silver nitrate. The corresponding changes of pCl^- in this region in the titration of chloride are read from the right-hand ordinates.

The changes of the ion exponents near the equivalence point are much more pronounced in the case of silver iodide than of silver chloride, since the solubility product of the former is about 10^6 times smaller than that of silver chloride. The values derived in the table and plotted in Figure 83 are actually found in potentiometric titrations, where pAg^+ is measured with the aid of a silver electrode.

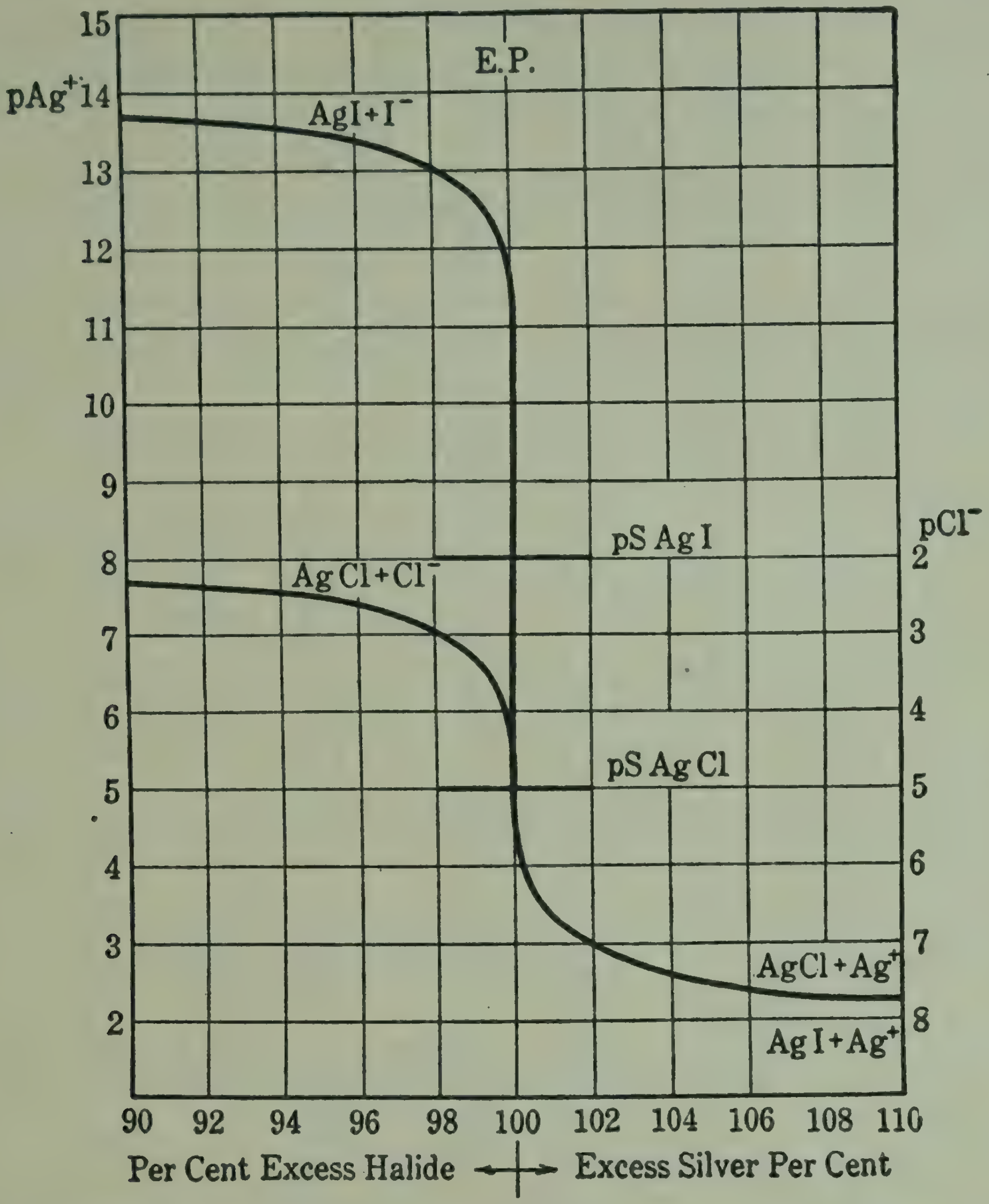


FIG. 83. Titration curves of 100 ml. 0.1 N sodium chloride and 100 ml. 0.1 N potassium iodide, respectively, with 0.1 N silver nitrate.

Determination of the end point.

Equal-turbidity method. No indicator is used in the determination of the end point in this method. Use is made of the fact that in the titration of sodium chloride with silver nitrate the solution is saturated with silver chloride at the equivalence point and then contains equal concentrations of silver and chloride ions. If a small amount of chloride or silver is added to a portion of the clear supernatant liquid, the latter will become turbid, owing to the formation of silver chloride, since the solubility of the silver chloride is decreased by an excess of either of the two ions. At the equivalence point the turbidity obtained with a slight excess of silver in the sample of the supernatant liquid is equal to that produced by an equal excess of chloride. If chloride were still in excess, the turbidity produced in a sample of the supernatant liquid by silver would be more intense than that produced by an excess of chloride; and the reverse effect would be noticed if silver nitrate had been added in excess during the titration. Therefore in applying this method, two equal portions of the clear supernatant liquid are withdrawn near the equivalence point and tested with silver nitrate and with chloride. If equally strong turbidities are not found, the titration is continued with chloride or silver nitrate to the point of equal turbidities. The *equal-turbidity method* was introduced more than one hundred years ago by Gay Lussac [1] for the determination of silver with chloride. The method, under the proper conditions, is one of the most exact of all titrimetric methods. It is of lasting significance for the atomic-weight determinations of silver, chlorine, and *metals analyzed in the form of pure metal chlorides*,[2] and is still used for the determination of silver in the mints of certain governments.

If the silver salt formed is very slightly soluble, as is the case with silver bromide, thiocyanate, and iodide, the saturated solution at the equivalence point contains so little of the dissolved salt that no turbidity is noticed with an excess of either of the two common ions. In such cases the end point can be found in a simpler way than described above. In the titration of bromide, for example, with silver nitrate, small portions of the clear supernatant liquid are withdrawn near the equivalence point and tested with silver for the presence of an excess of bromide. A turbidity will be produced as long as there is an excess of bromide present. The titration is carefully continued until no turbidity is produced by the addition of silver to the supernatant liquid.

Titration to the clear point. Various slightly soluble salts remain in colloidal solution during titration. This is especially the case in the determination of an alkali iodide with silver nitrate. Upon addition of the latter to the iodide solution, the silver iodide formed remains in colloidal solution, the particles being negatively charged by adsorption of iodide ions at their surface (see Chapter VII, p. 93). Near the equivalence point most of the iodide in the solution has been transformed into silver iodide, and upon further addition of silver nitrate the reagent will react with the adsorbed iodide. The stability of the suspension then decreases, owing to the removal of the peptizing iodide ions, and flocculation of the sol begins just before the equivalence point is reached. Still the supernatant liquid is turbid as long as some iodide remains in the adsorbed state. After all of the adsorbed iodide has reacted, the supernatant liquid becomes perfectly clear, and the end point is then reached. This "clear point" determination is very sharp and can be made with great precision.

---

[1] Gay Lussac, *Instruction sur l'essai des matières d'argent par la voie humide*, Paris, 1832.

[2] See, e.g., T. W. Richards and R. G. Wells, J. Am. Chem. Soc. *27*, 459 (1905); C. R. Johnson, J. Phys. Chem. *35*, 540, 830, 2237 (1931).

Use of potassium chromate as indicator for the detection of an excess of silver. The Mohr titration. In the above methods no indicator is required for the determination of the end point. In the titration of chloride with silver nitrate, potassium chromate is frequently used as an indicator. This is the well-known Mohr [1] method for the determination of chloride and bromide. Chromate ions combine with the silver to form slightly soluble red silver chromate at the end point. The conditions during the titration must be such that the chloride is precipitated quantitatively as silver chloride before the precipitation of the reddish silver chromate is perceptible. On the other hand the indicator should be sufficiently sensitive to give a sharp color change with a slight excess of silver.

We are dealing here with a case of fractional precipitation, the general theory of which has been discussed on page 65.

At the point where both solid phases, silver chloride and silver chromate, are in equilibrium with the solution we have

$$[\mathrm{Ag^+}][\mathrm{Cl^-}] = S_{\mathrm{AgCl}} = 10^{-10} \qquad [\mathrm{Ag^+}] = \frac{S_{\mathrm{AgCl}}}{[\mathrm{Cl^-}]}$$

$$[\mathrm{Ag^+}]^2[\mathrm{CrO_4^{=}}] = S_{\mathrm{Ag_2CrO_4}} = 2 \times 10^{-12} \quad [\mathrm{Ag^+}] = \sqrt{\frac{S_{\mathrm{Ag_2CrO_4}}}{[\mathrm{CrO_4^{=}}]}}.$$

At the point where silver chromate starts to precipitate and the indicator shows the end point, we have therefore

$$[\mathrm{Ag^+}] = \frac{S_{\mathrm{AgCl}}}{[\mathrm{Cl^-}]} = \sqrt{\frac{S_{\mathrm{Ag_2CrO_4}}}{[\mathrm{CrO_4^{=}}]}}$$

and $$\frac{[\mathrm{Cl^-}]}{\sqrt{[\mathrm{CrO_4^{=}}]}} = \frac{S_{\mathrm{AgCl}}}{\sqrt{S_{\mathrm{Ag_2CrO_4}}}} = \frac{10^{-10}}{\sqrt{2 \times 10^{-12}}} = 7 \times 10^{-5}.$$

At the equivalence point $[\mathrm{Cl^-}] = 10^{-5}$. If silver chromate starts to precipitate at this chloride-ion concentration,

$$[\mathrm{CrO_4^{=}}] = \left(\frac{[\mathrm{Cl^-}]}{7 \times 10^{-5}}\right)^2 = \frac{10^{-10}}{49 \times 10^{-10}} = 0.02.$$

---

[1] Fr. Mohr, Ann. d. Chem. *97*, 335 (1856).

Theoretically, therefore, the indicator will barely give silver chromate at the equivalence point when the chromate concentration of the solution is 0.02 molar. However it should be realized that a certain excess of silver must be added before the red silver chromate is visible.

Practically, an indicator concentration at the end point corresponding to about 5×10^{-3} molar chromate has proved to be satisfactory. Theoretically the indicator should change color when

$$[\mathrm{Cl}^-] = 7 \times 10^{-5} \sqrt{[\mathrm{CrO}_4^=]} = 7 \times 10^{-5} \times 7 \times 10^{-2} = 0.5 \times 10^{-5},$$

which is slightly beyond the theoretical end point, and the silver-ion concentration would then be

$$[\mathrm{Ag}^+] = \sqrt{\frac{2 \times 10^{-12}}{5 \times 10^{-3}}} = 2.0 \times 10^{-5}.$$

Actually the sensitivity of the indicator for silver ions is smaller, since a certain amount of silver chromate must be formed before it is visible. Experimentally this sensitivity is determined by adding 0.01 *N* silver nitrate from a micro buret to 100 ml. of 0.01 molar potassium chromate until a distinct difference in color is noticed when compared with a blank. At 25° the sensitivity corresponds to a silver-ion concentration of from 3.5 to 4×10^{-5} molar.

At 25° the sensitivity of 4×10^{-5} *N* silver is equal to the indicator blank; the sensitivity is unaffected by the presence of the white silver chloride. In the titration of 100 ml. of 0.1 *N* chloride with 0.1 *N* silver nitrate, the color change is not observed until the silver-ion concentration is 4×10^{-5} (in a volume of 200 ml.). This corresponds to an excess of 0.08 ml. of 0.1 *N* silver nitrate, or to a titration error of 0.08 per cent, which is negligibly small. The titration error, however, increases with increasing dilution of the chloride. If the titration is carried out with 0.01 *N* solution, the titration error amounts to 0.8 per cent. In the titration of dilute solutions the indicator blank should be determined separately and subtracted from the amount of standard solution used.

The Mohr method is generally used for the determination of chloride and bromide. It cannot be applied to the accurate determination of iodide and thiocyanate, for the end point is obscured as a result of adsorption phenomena.

The titration must be carried out in neutral or weakly alkaline solution. The pH should be greater than 7 but not larger than 10.5, as in acid medium the sensitivity of the indicator decreases very strongly with the hydrogen-ion concentration. The second ionization constant of chromic acid is small, and therefore the chromate ions react with hydrogen ions:

$$CrO_4^{=} + H^+ \rightleftarrows HCrO_4^-$$

and the decrease of the sensitivity is thus explained. On the other hand, the solution should not be too alkaline, since silver hydroxide might then precipitate before silver chromate. Sodium bicarbonate or borax is very useful for the adjustment of the acidity in the Mohr titration.

End-point detection with adsorption indicators. In a discussion of the properties of colloidal systems it was mentioned (p. 95) that suspensions of silver chloride or silver iodide in the presence of an excess of the halide ion acquire a negative charge owing to the adsorption of the latter, whereas the charge becomes positive in the presence of an excess of silver ions:

$$[AgClCl^-] \vdots K^+ \qquad \text{(negatively charged)}$$
$$[AgClAg^+] \vdots NO_3^- \qquad \text{(positively charged).}$$

A precipitate has a tendency to adsorb its own ions. Therefore silver chloride suspended in a medium containing chloride ions and other anions will in general tend to adsorb the chloride ions. As soon as the equivalence point is reached in an argentimetric chloride determination, part of the excess silver nitrate added will be adsorbed by the silver chloride particles. The nitrate ions are not strongly held by the particles; and if other anions are present which are more strongly adsorbed, they will take the position of the adsorbed nitrate ions.

The above explains the principle of the application of *adsorption indicators. These indicators do not give a color change in the solution but on the surface of the precipitate.* When a few drops of a dilute fluorescein solution are added to a 0.05 N silver nitrate solution the color of the indicator remains the same as in water. The fluorescein, therefore, does not behave as an indicator for dissolved silver ions. If a little chloride is added to the silver solution, silver chloride is formed; and the color turns red or pinkish, since the silver chloride adsorbs silver ions and the latter attract the fluorescein ions to the surface with the formation of the red silver fluoresceinate at the *surface* of the precipitate. If more chloride is added, the suspension remains red until chloride is in excess. At this point the silver originally adsorbed at the surface is transformed into silver chloride, and the particles will adsorb chloride ions. The suspension will then have the white color of silver chloride; and the fluorescein ions, adsorbed in the red form in the presence of an excess of silver, are sent into the solution, in which they have a yellowish-green color.[1]

Lecture experiment: Add to 50 ml. of approximately 0.02 *N* silver nitrate a few drops of a 0.1 per cent fluorescein solution in alcohol. Then add a few drops of 0.1 *N* sodium chloride. The color turns red and remains red upon further addition of chloride, until an excess has been added.

Fluorescein and dichlorofluorescein are very useful indicators in the titration of halides with silver nitrate. The following phenomena are usually observed during the titration: The silver halide remains partly in colloidal solution until the equivalence point is approached. About 1 per cent before the end point, flocculation occurs. The titration should then be continued carefully with vigorous agitation, until the precipitate appears reddish. Such a titration should not be carried out in direct sunlight, since silver halides with adsorbed indicator are extremely light-sensitive. The red color changes rapidly to gray and black in strong light.

Since the color change takes place on the surface of the particles, it is of importance to have as large a surface development of the precipitate as possible. Therefore the method works best under those conditions in which the precipitate separates as a flocculated colloid. Large amounts of neutral salts obscure the end point somewhat, because they exert their flocculating effect before the end point is reached. With very dilute halide solutions the amount of precipitate formed is so small that the color change is no longer pronounced. For this reason chloride solutions more dilute than 0.005 *N* cannot be titrated with fluorescein or dichlorofluorescein as indicator.

Fluorescein itself is a very weak acid with an ionization constant of the order of 10^{-8}. The color change is to be attributed to an adsorption of fluorescein ions; and therefore it may be expected that hydrogen ions will interfere, because they remove the indicator ions from the solution. This is actually true: titrations with fluorescein as indicator must be carried out in neutral or slightly alkaline medium (pH between 7 and 10). Dichlorofluorescein[1] is a stronger acid than fluorescein, and for this reason it can be used in slightly acid solutions. It is a very useful indicator in the titration of chlorides.

---

[1] See K. Fajans and O. Hassel, Z. Elektrochem. *29*, 495 (1923); K. Fajans and W. Steiner, Z. physik. Chem. *125*, 309 (1927); K. Fajans and H. Wolff, Z. anorg. allgem. Chem. *137*, 221 (1924); O. Hassel, Kolloid Z. *34*, 304 (1924); for review see I. M. Kolthoff, Chem. Rev. *16*, 87 (1935)

Bromides, iodides, and thiocyanates are better titrated with eosin (tetrabromfluorescein) as indicator. The color change to red is extremely sharp; the method gives excellent results, even in highly diluted solutions. Eosin is a much stronger acid than fluorescein, and therefore titrations can be made in solutions with a pH of 2 or greater. Unfortunately, eosin cannot be used in the chloride titration because the adsorbability of the eosinate ions by the silver halides is much greater than that of the fluoresceinate. We have seen that a silver chloride suspension in a solution containing an excess of chloride ions adsorbs the latter on the surface of the particles. If eosin is added to such a suspension, there will be a competition between the chloride and eosin ions to be adsorbed, and the result is that part of the adsorbed chloride is replaced by eosin. This causes a color change towards red. Therefore in the titration of chloride with silver nitrate, eosin cannot be used as an adsorption indicator, because the color will turn reddish long before the equivalence point is reached.[2]

Titration of silver with thiocyanate. The Volhard method for the determination of halides.

Silver can be determined very accurately in acid medium with potassium or ammonium thiocyanate as the precipitant. Silver thiocyanate is a very slightly soluble salt, having a solubility product of 7×10^{-13}. An excess of thiocyanate can be detected very sharply with a ferric salt, the latter forming the intensely colored red complex ferric thiocyanate in acid medium. The indicator is very sensitive towards an excess of thiocyanate. One to two ml. of a saturated solution of ferric ammonium sulfate (about 40 per cent) added to 100 ml. of 0.2–0.5 *N* nitric acid produces a pale orange color with 0.01 ml. of 0.1 *N* thiocyanate and changes to red-orange with a larger excess. The indicator blank therefore is negligibly small.

---

[1] I. M. Kolthoff, W. M. Lauer, and C. J. Sunde, J. Am. Chem. Soc. *51*, 3273 (1929).

[2] For further details concerning the use and application of various other dyes as adsorption indicators, the student is referred to I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis*, Vol. II; on the mechanism of the color change with adsorption indicators, see I. M. Kolthoff, Kolloid Z. *68*, 190 (1934).

In the titration of silver with thiocyanate in acid medium, using ferric iron as an indicator, the color change appears 0.7 to 1 per cent before the equivalence point. The silver thiocyanate formed adsorbs silver ions, which are removed from the solution. Therefore after the first end point has been reached, the titration must be continued with vigorous agitation until the orange color does not disappear, even after strong shaking. Then all of the adsorbed silver is transformed into the thiocyanate, and highly accurate results are obtained.

An important application of this silver titration is made in the determination of chloride, and also of bromide and iodide in acid medium. The halides cannot be titrated in strongly acid medium by Mohr's method or by the use of adsorption indicators. Therefore an excess of standard silver nitrate is added to the solution and the excess is back-titrated with standard thiocyanate. This is the well-known *Volhard* method.[1]

In the chloride determination according to Volhard, a difficulty is encountered in the back-titration of the excess of silver:

$$\begin{aligned} \mathrm{Cl^-} + \mathrm{Ag^+}\ (\text{excess}) &\rightleftarrows \mathrm{AgCl} \\ \mathrm{Ag^+} + \mathrm{CNS^-} &\rightleftarrows \mathrm{AgCNS.} \end{aligned}$$

Therefore we have here two slightly soluble salts, AgCl and AgCNS, in equilibrium with the solution. Hence the following relation holds:

$$\frac{[\mathrm{Cl^-}]}{[\mathrm{CNS^-}]} = \frac{S_{\mathrm{AgCl}}}{S_{\mathrm{AgCNS}}} = \frac{1.12 \times 10^{-10}}{7 \times 10^{-13}} = 160.$$

After all the silver has been titrated back, an excess of thiocyanate may react with the silver chloride, since silver thiocyanate is less soluble than silver chloride:

$$\mathrm{AgCl} + \mathrm{CNS^-} \rightleftarrows \mathrm{AgCNS} + \mathrm{Cl^-}.$$

Equilibrium is established when $\frac{[\mathrm{Cl^-}]}{[\mathrm{CNS^-}]}$ has become equal to 160 or, in other words, after practically all of the excess thiocyanate has reacted. The end point, therefore, is not very sharp.

Let us take, by way of illustration, a case in which 100 ml. of a silver chloride suspension is treated with 0.1 ml. of 0.1 *N* thiocyanate, corresponding to a concentration of 10^{-4}. After equilibrium is established:

---

[1] J. Volhard, J. prakt. Chem. *117*, 217 (1874).

$$[\mathrm{Cl}^-] = \frac{160}{161} \times 10^{-4}$$

and

$$[\mathrm{CNS}^-] = \frac{1}{161} \times 10^{-4}.$$

The sensitivity of the ferric indicator towards thiocyanate corresponds to a concentration of 10^{-5} *N* of the latter. Therefore, according to this calculation, it will be necessary to add an excess of 1.60 ml. of 0.1 *N* thiocyanate before a permanent end point is obtained. Experimentally it is found that this excess amounts to 2.5 ml. of 0.1 *N* thiocyanate.

This reaction between silver chloride and the excess of thiocyanate is relatively slow. Rothmund and Burgstaller[1] have recommended that the aqueous suspension be covered with a layer of ether, benzene, ligroin, or any other organic solvent immiscible with water. The silver chloride agglomerates at the water-organic solvent interface and is withdrawn from the action of the thiocyanate solution. This method gives fair results. Excellent results, however, are obtained if about 1 ml. of nitrobenzene is added to the suspension before back-titrating the excess of silver. A sharp and permanent end point was found by Caldwell[2] under these conditions, and the authors were able to confirm the results.

One can also proceed in the following way: Near the end point in the back-titration, the precipitate is allowed to settle, and a little more thiocyanate is then added to the clear supernatant liquid. If the color does not change, the whole is well stirred and the precipitate is allowed to settle again. The titration is continued until a color change is noticed in the supernatant liquid. Not all the silver has reacted at this point, since part of it is adsorbed by the precipitate. Therefore, after reaching the first end point, the mixture is shaken or stirred vigorously. The reddish color disappears, and the titration is continued until a color change occurs again in the supernatant liquid. This method gives results accurate to about 0.5 per cent. Caldwell's procedure, however, is preferable. Another alternative is to add an excess of silver nitrate to the acid chloride solution, make up to the mark in a volumetric flask, and titrate an aliquot part of the clear supernatant liquid or the filtrate with thiocyanate. The advantage of the filtration method is that a sharp and permanent end point is obtained.

---

[1] V. Rothmund and A. Burgstaller, Z. anorg. Chem. *63*, 330 (1909).
[2] J. R. Caldwell, Ind. Eng. Chem., Anal. Ed. *7*, 38 (1935).

In the titration of bromide according to Volhard, no difficulties are encountered in the determination of the end point because silver bromide is slightly less soluble than silver thiocyanate. Iodide also can be determined very accurately by the Volhard method. In this case one should not add the iron indicator until there is an excess of silver, because dissolved iodide reacts with ferric iron with the liberation of iodine:

$$Fe^{+++} + I^- \rightleftarrows Fe^{++} + \tfrac{1}{2} I_2.$$

Titration of cyanide with silver nitrate. Complex formation.

When silver ions are added to a solution of alkali cyanide, a very stable complex cyanide is formed:

$$Ag^+ + 2\,CN^- \rightleftarrows Ag(CN)_2^- \qquad (1)$$

the alkali salt of which is soluble. After the above reaction is complete, further addition of silver nitrate results in the formation of a precipitate of silver silvercyanide, usually called silver cyanide:

$$Ag^+ + Ag(CN)_2^- \rightarrow Ag[Ag(CN)_2] \text{ (end point).}$$

Therefore the end point is marked by the appearance of a turbidity.

$$\frac{[Ag^+][CN^-]^2}{[Ag(CN)_2^-]} = 10^{-21}. \qquad (2)$$

Let us assume that at the end point the concentration of the complex $KAg(CN)_2$ is 0.05 molar. Then, since at this point (see equation 1)

$$[Ag^+] = \tfrac{1}{2}[CN^-] \quad \text{or} \quad [CN^-] = [2\,Ag^+],$$

we find that

$$\frac{4[Ag^+]^3}{0.05} = 10^{-21}$$

and

$$[Ag^+] = \sqrt[3]{\frac{5 \times 10^{-23}}{4}} \doteq 2.3 \times 10^{-8}. \qquad (3)$$

The solubility product of silver silvercyanide is

$$[Ag^+][Ag(CN)_2^-] = 2 \times 10^{-12}. \qquad (4)$$

Therefore the precipitation of silver silvercyanide begins when

$$[Ag^+] \geqq \frac{2 \times 10^{-12}}{[Ag(CN)_2^-]} \geqq \frac{2 \times 10^{-12}}{5 \times 10^{-2}} \geqq 4 \times 10^{-11}. \qquad (5)$$

This means, then, that the turbidity will appear just before the stoichiometric end point is reached. If in the titration of 100 ml. of 0.2 M potassium cyanide, 99.9 ml. of 0.1 N silver nitrate have been added, the amount of cyanide left in the solution corresponds to 0.1 ml. of 0.2 molar solution in 200 ml. or to a concentration of 10^{-4}. Then, according to equation (2),

$$[\mathrm{Ag^+}] = \frac{[\mathrm{Ag(CN)_2^-}]}{[\mathrm{CN^-}]^2} \times 10^{-21} = \frac{5 \times 10^{-2}}{10^{-8}} \times 10^{-21} = 5 \times 10^{-15},$$

whereas precipitation of silver silvercyanide begins when the silver-ion concentration is equal to, or greater than, 4×10^{-11} (equation 5). Therefore the titration error is smaller than 0.1 per cent, since after the addition of 99.9 per cent of silver nitrate the solution is still clear and the turbidity will appear between this point and the equivalence point.

This method, originally proposed by Liebig,[1] yields good results, especially when the reagent is added very carefully near the end point. Ammonia will interfere, of course, since it combines with silver ions to form a complex (p. 60) and keeps the silver silvercyanide in solution. Dénigès [2] therefore recommended the detection of the end point with potassium iodide and performed the titration in ammoniacal medium. The amounts of ammonia and iodide added must be carefully regulated, for otherwise the end point may appear too early or too late.[3] With the proper amounts of both, the end point can be determined very accurately and is found to lie very close to the *equivalence point* (for procedure, see p. 574).

In these titrations the equivalent weight of cyanide is twice the molecular weight.

Formation of slightly dissociated compounds with mercuric nitrate or mercuric perchlorate.

Determination of chloride and bromide with mercuric nitrate in acid medium. Mercuric chloride and bromide are only slightly dissociated in solution:

$$\mathrm{Hg^{++}} + 2\,\mathrm{Cl^-} \rightleftarrows \mathrm{HgCl_2}$$
$$\mathrm{Hg^{++}} + 2\,\mathrm{Br^-} \rightleftarrows \mathrm{HgBr_2}.$$

Upon addition of a well-ionized mercuric salt, such as mercuric nitrate or perchlorate, to a solution of chloride or bromide, mercuric ions disappear because of the formation of the slightly dissociated mercuric halides. A substance which reacts visibly with mercuric ions is used as an indicator to detect the end point. As such, *sodium nitroprusside* is suitable; it yields slightly soluble mercuric nitroprusside with mercuric ions but does not react with mercuric chloride or mercuric bromide. The end point therefore is marked by the appearance of a turbidity due to precipitated mercuric nitroprusside. In the titration of chlorides there is a small indicator correction which can be determined experimentally. It increases slightly with the amount of mercuric chloride present at the end of the titration, since the latter removes part of the excess mercuric ions with the formation of a complex:

---

[1] J. von Liebig, Ann. d. Chem. *77*, 102 (1851).

[2] G. Dénigès, Compt. rend. *117*, 1078 (1893).

[3] See I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis*, Vol. II.

$$HgCl_2 + Hg^{++} \rightleftarrows 2\,HgCl^+.$$

The method is of great practical importance, since it allows a direct titration of chloride in an acid medium. It cannot be applied to the determination of iodide, because mercuric iodide is slightly soluble and has an intense red color. In this particular case use can be made of the property possessed by the iodide of forming a fairly stable complex with mercury:

$$Hg^{++} + 4\,I^- \rightleftarrows HgI_4^=. \qquad (1)$$

The end point is indicated by the appearance of a permanent red turbidity of mercuric iodide:

$$HgI_4^= + Hg^{++} \rightleftarrows 2\,HgI_2. \qquad (2)$$

The end point appears too early owing to the dissociation of the complex ion into mercuric and iodide ions (reaction 1 from right to left). The titration error can be computed from the complex constant of $HgI_4^=$ and the solubility product of HgI_2;[1] it can also be experimentally determined.

Application of the reaction $Hg^{++} + 2\,CNS^- \rightleftarrows Hg(CNS)_2$.

Mercuric thiocyanate is very slightly dissociated. In the titration of a mercuric salt with thiocyanate, the ions of the latter are removed by the formation of slightly dissociated mercuric thiocyanate. When the reaction is complete, an excess of the thiocyanate reacts with the ferric iron which is added as an indicator (p. 475).

If the concentration of the mercury salt is large, a precipitate of mercuric thiocyanate is formed just before the end point. The precipitate, however, does not interfere with the color change The latter is very sharp and the indicator blank is negligibly small when the temperature is below 20°.

The method affords a simple and accurate determination of mercuric mercury in acid solutions. It can also be applied to the titration of thiocyanate with a standard mercury solution. In the latter case mercuric nitrate solution is added to the acid thiocyanate solution, until the reddish brown color of the complex ferric thiocyanate changes to colorless. This determination is applied in the titration of cyanides. Mercuric cyanide is much less dissociated than mercuric thiocyanate. Therefore an excess of standard mercuric nitrate may be added to the cyanide solution and the excess back-titrated with thiocyanate.

---

[1] See I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis*, Vol. I.

In all these cases chlorides and bromides interfere, since they form slightly dissociated mercuric salts.

PROBLEMS

1. Calculate the bromide- and silver-ion concentrations in the titration of 100 ml. of 0.1 *N* potassium bromide with 0.1 *N* silver nitrate after addition of 50, 90, 98, 99, 99.8, 99.9, 100.00, 100.1, 100.2, 101, and 110 ml. of the reagent. ($S_{AgBr} = 4 \times 10^{-13}$.)

2. What is the bromide-ion concentration in a 0.01 molar potassium chromate solution in equilibrium with solid AgBr and Ag_2CrO_4? ($S_{AgBr} = 4 \times 10^{-13}$; $S_{Ag_2CrO_4} = 2 \times 10^{-12}$.) *Ans.* 3×10^{-8} molar.

3. What is the solubility of silver oxalate, $Ag_2C_2O_4$, in a solution which is 0.01 *N* with respect to silver ions? ($S_{Ag_2C_2O_4} = 5 \times 10^{-12}$.) *Ans.* 5×10^{-8} molar.

4. What is the ratio of $[Br^-]$ to $[CNS^-]$ in a solution in equilibrium with solid AgBr and AgCNS? ($S_{AgBr} = 4 \times 10^{-13}$; $S_{AgCNS} = 7 \times 10^{-13}$.) *Ans.* $[Br^-] : [CNS^-] = 0.57$.

5. Describe the difference in the mechanism of the indicator action of the following indicators: fluorescein (adsorption indicator); chromate (in the Mohr titration); ferric sulfate in the Volhard titration; sodium nitroprusside in the titration of chloride with mercuric nitrate.

6. 50.00 ml. of a potassium cyanide solution require 20.00 ml. of 0.1100 *N* silver nitrate in a titration according to Denigès. How much cyanide does the solution contain? Can the titration be carried out in the presence of chloride? *Ans.* $[CN^-] = 0.0880$ molar.

7. 25.00 ml. of a sodium chloride solution are titrated according to Volhard by adding 50.00 ml. of 0.1100 *N* silver nitrate solution and diluting the mixture to 100 ml.; 50 ml. of the supernatant liquid require 5.23 ml. of 0.0980 *N* thiocyanate. How much sodium chloride does the solution contain? Make the same calculation, but correct for the amount of silver nitrate adsorbed by the silver chloride, assuming that this adsorption amounts to 0.1 ml. of 0.1100 *N* silver nitrate. *Ans.* 0.2615 g. NaCl, uncorrected; 0.2609 g. NaCl, corrected.

8. The silver salt AgA of an organic acid has a solubility in water of 10^{-3} *M*. To 25 ml. of 0.1 *N* solution of the sodium salt of this organic acid are added 25 ml. of 0.12 *N* silver nitrate. (a) What is the solubility of AgA after the addition of silver nitrate? (b) What is the percentage of organic ion not precipitated? *Ans.* (a) 10^{-4} *M*; (b) 0.2 per cent.

9. A 0.1 *M* solution of alkali iodate is titrated with 0.1 *N* silver nitrate, chromate being used as an indicator. The chromate concentration at the end point is 2×10^{-3} *M*. Solubility product of silver iodate is 2×10^{-8}, of silver chromate 2×10^{-12}. Calculate (a) the concentration of iodate at the end point; (b) the titration error. *Ans.* (a) $[IO_3] = 10^{-3}$; (b) -2 per cent.

CHAPTER XXXI

THEORY OF OXIDATION-REDUCTION REACTIONS

The oxidation potential.

A process in which an electron transfer takes place is called an *oxidation-reduction* process, a substance giving off electrons being oxidized and a substance taking up electrons being reduced. In other words, an oxidizing agent combines with electrons and is thereby reduced, whereas a reducing agent furnishes electrons:

$$\mathrm{Fe}^{+++} + e \rightleftarrows \mathrm{Fe}^{++}$$

$$\mathrm{Ce}^{++++} + e \rightleftarrows \mathrm{Ce}^{+++}$$

$$\mathrm{Sn}^{++++} + 2\,e \rightleftarrows \mathrm{Sn}^{++}$$

or, in general,

$$\underset{\textit{(oxidized form)}}{\mathrm{Ox}} + n\,e \rightleftarrows \underset{\textit{(reduced form)}}{\mathrm{Red.}}$$

In any oxidation-reduction reaction there are always two oxidation-reduction systems involved, one furnishing the electrons and the other combining with the electrons. In the oxidation of ferrous iron by ceric cerium, we have the two partial reactions:

$$\begin{array}{c} \mathrm{Fe}^{++} \rightleftarrows \mathrm{Fe}^{+++} + e \\ \mathrm{Ce}^{++++} + e \rightleftarrows \mathrm{Ce}^{+++} \\ \hline \mathrm{Fe}^{++} + \mathrm{Ce}^{++++} \rightleftarrows \mathrm{Fe}^{+++} + \mathrm{Ce}^{+++}. \end{array}$$

The *intensity* of the oxidizing or reducing action of a system is determined by its *oxidation potential.* If a piece of a noble metal, such as platinum, gold, or palladium, be placed in a solution of an oxidant and its reduced form, there will be established a potential difference between the electrode and the solution, the magnitude of which is determined by the particular system itself and by the ratio of the oxidized to the reduced form. This potential is called the oxidation potential.

If we are dealing with a simple system,

$$\mathrm{Ox} + n\,e \rightleftarrows \mathrm{Red},$$

the oxidation potential E is

$$E = E_o + \frac{0.060}{n} \log \frac{[\mathrm{Ox}]}{[\mathrm{Red}]}. \qquad (30°;\ \text{see p. 147}) \qquad (1)$$

E_o is a characteristic constant of each system and represents the oxidation potential in a system in which $[\mathrm{Ox}] = [\mathrm{Red}]$. The second term in equation (1), $\frac{0.060}{n} \log \frac{[Ox]}{[Red]}$, then becomes equal to 0, and

$$E = E_o.$$

E_o is called the normal potential of the system. Normal potentials of various systems are given in Table LXIV. They are expressed

TABLE LXIV. NORMAL POTENTIALS OF SOME OXIDIZING-REDUCING SYSTEMS

OXIDIZED FORM	REDUCED FORM	ELECTRODE REACTION	E_o
			(Volts)
MnO_4^-	MnO_2	$MnO_4^- + 4H^+ + 3e \rightleftharpoons MnO_2 + 2H_2O$	$+1.59$ (at $[H^+] = 1$)
MnO_4^-	Mn^{++}	$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{++} + 4H_2O$	$+1.50$ (at $[H^+] = 1$)
Ce^{++++} [a]	Ce^{+++}	$Ce^{++++} + e \rightleftharpoons Ce^{+++}$	$+1.45$
PbO_2	Pb^{++}	$PbO_2 + 4H^+ + 2e \rightleftharpoons Pb^{++} + 2H_2O$	$+1.46$ (at $[H^+] = 1$)
BrO_3^-	Br_2	$2BrO_3^- + 12H^+ + 10e \rightleftharpoons Br_2 + 6H_2O$	$+1.45$ (at $[H^+] = 1$)
Cl_2	Cl^-	$Cl_2 + 2e \rightleftharpoons 2Cl^-$	$+1.4$
MnO_2	Mn^{++}	$MnO_2 + 4H^+ + 2e \rightleftharpoons Mn^{++} + 2H_2O$	$+1.35$ (at $[H^+] = 1$)
$Cr_2O_7^{=}$	Cr^{+++}	$Cr_2O_7^{=} + 14H^+ + 6e \rightleftharpoons 2Cr^{+++} + 7H_2O$	$+1.3$ (at $[H^+] = 1$)
O_2	H_2O	$O_2 + 4H^+ + 4e \rightleftharpoons 2H_2O$	$+1.23$ (at $[H^+] = 1$)
Tl^{+++}	Tl^+	$Tl^{+++} + 2e \rightleftharpoons Tl^+$	$+1.21$
Au^{+++}	Au^+	$Au^{+++} + 2e \rightleftharpoons Au^+$	$+1.2$
$VO_4^{\equiv}$	VO^{++}	$VO_4^{\equiv} + 6H^+ + e \rightleftharpoons VO^{++} + 3H_2O$	$+1.2$ (at $[H^+] = 1$)
IO_3^-	I_2	$2IO_3^- + 12H^+ + 10e \rightleftharpoons I_2 + 6H_2O$	$+1.19$ (at $[H^+] = 1$)
Br_2	Br^-	$Br_2 + 2e \rightleftharpoons 2Br^-$	$+1.08$
Fe^{+++}	Fe^{++}	$Fe^{+++} + e \rightleftharpoons Fe^{++}$	$+0.76$
BrO_3^-	Br^-	$BrO_3^- + 3H_2O + 6e \rightleftharpoons Br^- + 6OH^-$	$+0.60$
H_3AsO_4	H_3AsO_3	$H_3AsO_4 + 2H^+ + 2e \rightleftharpoons H_3AsO_3 + H_2O$	$+0.58$ (at $[H^+] = 1$)
I_2	I^-	$I_2 + 2e \rightleftharpoons 2I^-$	$+0.58$
$Fe(CN)_6^{\equiv}$	$Fe(CN)_6^{----}$	$Fe(CN)_6^{\equiv} + e \rightleftharpoons Fe(CN)_6^{----}$	$+0.4$
VO^{++}	V^{+++}	$VO^{++} + 2H^+ + e \rightleftharpoons V^{+++} + H_2O$	$+0.4$ (at $[H^+] = 1$)
Sn^{++++}	Sn^{++}	$Sn^{++++} + 2e \rightleftharpoons Sn^{++}$	$+0.2$
Cu^{++}	Cu^+	$Cu^{++} + e \rightleftharpoons Cu^+$	$+0.17$
H^+	H_2	$2H^+ + 2e \rightleftharpoons H_2$	0.00
Ti^{++++}	Ti^{+++}	$Ti^{++++} + e \rightleftharpoons Ti^{+++}$	-0.04
V^{+++}	V^{++}	$V^{+++} + e \rightleftharpoons V^{++}$	-0.2
Cr^{+++}	Cr^{++}	$Cr^{+++} + e \rightleftharpoons Cr^{++}$	-0.4
S	$S^{=}$	$S + 2e \rightleftharpoons S^{=}$	-0.70

[a] As sulfate in 1 to 4 N sulfuric acid.

in volts and are referred to the normal hydrogen electrode as the standard reference electrode. The oxidation potential of a mixture of ferric and ferrous iron, for example, is given by

$$\mathrm{Fe^{+++}} + e \rightleftarrows \mathrm{Fe^{++}}$$

$$n = 1$$

$$E = E_o + 0.060 \log \frac{[\mathrm{Fe^{+++}}]}{[\mathrm{Fe^{++}}]} \quad (30°)^{1} \tag{2}$$

The oxidation potential increases with an increase in the value of the ratio of $[\mathrm{Fe^{+++}}]$ to $[\mathrm{Fe^{++}}]$. If the ratio is 10, $E = E_o + 0.060 \log 10 = E_o + 0.060$; if it is 100, $E = E_o + 0.060 \log 100 = E_o + 0.120$; if it is $\frac{1}{10}$, $E = E_o + 0.060 \log \frac{1}{10} = E_o - 0.060$, etc. Sometimes it is possible to transform one of the two forms into a stable complex or a slightly soluble compound. This, of course, will greatly affect the oxidation potential. Ferric ions, for example, form a very stable complex with fluoride and also with phosphoric acid:

$$\mathrm{Fe^{+++}} + 6\,\mathrm{F^-} \rightleftarrows \mathrm{FeF_6^{\equiv}}.$$

Addition of fluoride to a mixture of ferric and ferrous iron reduces $[\mathrm{Fe^{+++}}]$ greatly; therefore the oxidation potential decreases as well, and the reducing power of the ferrous iron increases greatly. Ferric ions, for example, react with iodide:

$$\mathrm{Fe^{+++}} + \mathrm{I^-} \rightleftarrows \mathrm{Fe^{++}} + \tfrac{1}{2}\,\mathrm{I_2}.$$

However, by the addition of fluoride the ferric ions are removed in the form of a complex, and the oxidation potential is reduced to such a degree that no iodine is liberated in the mixture containing iodide. Phosphoric acid has qualitatively the same effect.

---

[1] As usual we have written concentrations instead of activities in equation (2). It would have been more exact to write equation (2) as follows:

$$E = E_o + 0.060 \log \frac{[\mathrm{Fe^{+++}}]f_{\mathrm{Fe^{+++}}}}{[\mathrm{Fe^{++}}]f_{\mathrm{Fe^{++}}}} \tag{2a}$$

in which $f_{\mathrm{Fe^{+++}}}$ represents the activity coefficient of the ferric ions and $f_{\mathrm{Fe^{++}}}$ that of the ferrous ions. Especially when the oxidized and reduced forms consist of ions of higher valence, the concentration and the kind of electrolyte present have a large effect upon the ratio of the activity coefficients of both forms and therefore also upon the oxidation potential. This is true, for example, in the following systems: ferrocyanide-ferricyanide, ferrous-ferric iron, cerous-ceric cerium. When dealing with such systems, it is of advantage to know the oxidation potential in a given medium, e.g., in 1 N sulfuric acid or 2 N perchloric acid. Such an oxidation potential is often called the *formal* oxidation potential. When the composition of the medium remains constant, equation (2) is strictly valid. E_o refers then to the formal oxidation potential in the particular medium.

Ceric cerium, which is a powerful oxidizing agent, is quantitatively reduced by iodide. However, if fluoride is added, the quadrivalent cerium ions are transformed into a stable complex and no longer react with iodide.

The oxidation potential of a potassium ferro-ferricyanide solution is given by

$$\mathrm{Fe(CN)}_6^{----} \rightleftarrows \mathrm{Fe(CN)}_6^{---} + e$$

$$E = E_o + 0.060 \log \frac{[\mathrm{Fe(CN)}_6^{---}]}{[\mathrm{Fe(CN)}_6^{----}]}. \qquad (30°)$$

If an excess of zinc sulfate is added to a mixture of the two, the ferrocyanide precipitates in the form of $K_2Zn_3[Fe(CN)_6]_2$, and the ferricyanide as $Zn_3[Fe(CN)_6]_2$. The former is much less soluble than the latter, and therefore the ratio of ferricyanide to ferrocyanide in the solution is greatly increased by the zinc salt; and consequently the oxidation potential is also increased.

From the above we see that it is possible to change the oxidation potential of a system over a wide range by transforming one of the two forms into a complex or slightly soluble compound.

In the reduction of many oxidizing agents which contain oxygen, the oxygen content is decreased during the reduction. In these cases the oxidation potential will also be a function of the hydrogen-ion concentration of the solution, since the latter ions take part in the reduction.

Examples:

$$\mathrm{MnO}_4^- + 8\,\mathrm{H}^+ + 5\,e \rightleftarrows \mathrm{Mn}^{++} + 4\,\mathrm{H_2O}$$

$$E_{\mathrm{MnO}_4^-} = E_{o_{\mathrm{MnO}_4^-}} + \frac{0.060}{5} \log \frac{[\mathrm{H}^+]^8[\mathrm{MnO}_4^-]}{[\mathrm{Mn}^{++}]} \qquad (30°)$$

$$\mathrm{Cr_2O_7^{=}} + 14\,\mathrm{H}^+ + 6\,e \rightleftarrows 2\,\mathrm{Cr}^{+++} + 7\,\mathrm{H_2O}$$

$$E_{\mathrm{Cr_2O_7^{=}}} = E_{o_{\mathrm{Cr_2O_7^{=}}}} + \frac{0.060}{6} \log \frac{[\mathrm{H}^+]^{14}[\mathrm{Cr_2O_7^{=}}]}{[\mathrm{Cr}^{+++}]^2}. \qquad (30°)$$

In these cases the equations do not hold rigorously. The reactions have been written as reversible reactions, which is not quite correct. Ions intermediate between permanganate and manganous manganese are formed during the reduction of the former, and the same is true in the reduction of dichromate to chromic chromium. Nevertheless, it is true that the hydrogen ions have an enormous effect upon the oxidation potential of the above oxidizing agents. At a pH of 6, for example, it is found that the oxidation potential of permanganate is about 0.6 volt lower than in 1 *N* acid solution ($\mathrm{pH} = 0$). Use is made of this fact, for example, in the fractional oxidation of the halides to free halogen. At a pH of 5 to 6 iodide is oxidized to iodine by permanganate, whereas bromide and chloride are not affected. At a pH of about 3 (acetic acid) bromide is oxidized, but chloride is still unattacked. The latter is oxidized only at a much higher hydrogen-ion concentration.

The reduction of vanadate and of uranyl ions is strictly reversible.

$$VO_3^- + 4\,H^+ + e \rightleftarrows VO^{++} + 2\,H_2O$$

$$E_{VO_3^-} = E_{oVO_3^-} + \frac{0.060}{1}\log\frac{[VO_3^-][H^+]^4}{[VO^{++}]}$$

$$E_{oVO_3^-} = 0.92 \text{ at } [H^+] = 1, \text{ and } [VO_3^-] = [VO^{++}].$$

At a pH of 1 then, the potential is reduced to

$$0.92 - 0.24 = 0.68 \text{ volt}$$

$$UO_2^{++} + 4\,H^+ + 2\,e \rightleftarrows U^{++++} + 2{\cdot}H_2O$$

$$E_{UO_2^{++}} = E_{oUO_2^{++}} + \frac{0.060}{2}\log\frac{[UO^{++}][H^+]^4}{[U^{++++}]}.$$

The change in the oxidation potential with the relative amounts of reducing and oxidizing agent during a titration.

In connection with the application of oxidation-reduction indicators (see p. 491) and also of indicators specific for one of the components, it is of importance to study the change in the oxidation potential during a titration of a reducing agent with an oxidant, or vice versa.

In the titration of a reducing agent with an oxidizing agent, both systems are in equilibrium; and hence the oxidation potentials of both must be the same. This allows us to calculate the ratio of $\frac{[Ox_1]}{[Red_1]}$ to $\frac{[Ox_2]}{[Red_2]}$, considering that the reaction is represented by the equation:

$$Ox_1 + Red_2 \rightleftarrows Red_1 + Ox_2. \qquad (3)$$

Let us take as an example the titration of ferrous iron with ceric cerium:

$$Ce^{++++} + Fe^{++} \rightleftarrows Ce^{+++} + Fe^{+++}. \qquad (4)$$

The oxidation potential of the ceric-cerous cerium system, E_{Ce}, is equal to that of the ferric-ferrous iron system, E_{Fe}, at equilibrium:

$$E_{Ce} = E_{oCe} + 0.060\log\frac{[Ce^{++++}]}{[Ce^{+++}]} \qquad (5)$$

$$E_{Fe} = E_{oFe} + 0.060\log\frac{[Fe^{+++}]}{[Fe^{++}]} \qquad (6)$$

$$E_{oCe} = +\,1.45;\ E_{oFe} = +\,0.76;$$

$$E_{Ce} = E_{Fe} \text{ (at equilibrium).}$$

Hence $$1.45 + 0.060\log\frac{[Ce^{++++}]}{[Ce^{+++}]} = 0.76 + 0.060\log\frac{[Fe^{+++}]}{[Fe^{++}]}$$

or $$\log\frac{[Fe^{+++}]}{[Fe^{++}]} = \frac{0.69}{0.060} + \log\frac{[Ce^{++++}]}{[Ce^{+++}]} = 11.5 + \log\frac{[Ce^{++++}]}{[Ce^{+++}]}$$

$$\log\frac{[Fe^{+++}]}{[Fe^{++}]} - \log\frac{[Ce^{++++}]}{[Ce^{+++}]} = 11.5$$

or $$\frac{[Fe^{+++}]}{[Fe^{++}]}\cdot\frac{[Ce^{+++}]}{[Ce^{++++}]} = 10^{11.5}. \qquad (7)$$

It is of importance to find the value of the oxidation potential at the equivalence point. This point is reached after the addition of 100 ml. of ceric cerium to 100 ml. of ferrous iron of the same normality.

According to equation (4) we have at the equivalence point

$$[\mathrm{Ce^{+++}}] = [\mathrm{Fe^{+++}}]$$

and

$$[\mathrm{Ce^{++++}}] = [\mathrm{Fe^{++}}]$$

or

$$\frac{[\mathrm{Ce^{++++}}]}{[\mathrm{Ce^{+++}}]} = \frac{[\mathrm{Fe^{++}}]}{[\mathrm{Fe^{+++}}]}. \tag{8}$$

Now

$$E_{\mathrm{Ce}} = E_{o\mathrm{Ce}} + 0.060 \log \frac{[\mathrm{Ce^{++++}}]}{[\mathrm{Ce^{+++}}]}$$

$$E_{\mathrm{Fe}} = E_{o\mathrm{Fe}} + 0.060 \log \frac{[\mathrm{Fe^{+++}}]}{[\mathrm{Fe^{++}}]}.$$

Adding, we obtain

$$2\,E = E_{o\mathrm{Ce}} + E_{o\mathrm{Fe}} + 0.060 \log \frac{[\mathrm{Ce^{++++}}]}{[\mathrm{Ce^{+++}}]}\,\frac{[\mathrm{Fe^{+++}}]}{[\mathrm{Fe^{++}}]}. \tag{9}$$

Equation (8) informs us that $\frac{[\mathrm{Ce^{++++}}]}{[\mathrm{Ce^{+++}}]}$ is the reciprocal value of $\frac{[\mathrm{Fe^{+++}}]}{[\mathrm{Fe^{++}}]}$.

In other words, at the equivalence point

$$\frac{[\mathrm{Ce^{++++}}]}{[\mathrm{Ce^{+++}}]}\,\frac{[\mathrm{Fe^{+++}}]}{[\mathrm{Fe^{++}}]} = 1,$$

and

$$0.060 \log \frac{[\mathrm{Ce^{++++}}]}{[\mathrm{Ce^{+++}}]}\,\frac{[\mathrm{Fe^{+++}}]}{[\mathrm{Fe^{++}}]} = 0.$$

Therefore at the equivalence point (equation 9)

$$2\,E = E_{o\mathrm{Ce}} + E_{o\mathrm{Fe}}.$$

The potential at the equivalence point is given by:

$$E = \frac{E_{o\mathrm{Ce}} + E_{o\mathrm{Fe}}}{2} = \frac{1.45 + 0.76}{2} = 1.105.$$

It now is a simple matter to calculate the change in the oxidation potential during the titration of ferrous iron with ceric cerium. Suppose that we titrate 100 ml. of 0.1 *N* ferrous iron with 0.1 *N* ceric cerium. After the addition of 9 ml. of the oxidizing agent, we have

$$\frac{[\mathrm{Fe^{+++}}]}{[\mathrm{Fe^{++}}]} = \frac{9}{91} = \frac{1}{10}, \text{ approximately,}$$

and

$$E = 0.76 + 0.060 \log \frac{[\mathrm{Fe^{+++}}]}{[\mathrm{Fe^{++}}]} = 0.76 - 0.060 = 0.70.$$

After the addition of 99 ml. of ceric cerium

$$\frac{[\mathrm{Fe^{+++}}]}{[\mathrm{Fe^{++}}]} = 100$$

and

$$E = 0.76 + 0.060 \log \frac{100}{1} = 0.76 + 0.120 = 0.88.$$

At the equivalence point $E = 1.105$. When there is an excess of ceric cerium, the oxidation potential is calculated from the ratio of ceric cerium to cerous cerium and the normal potential, 1.45, of this system. For example, after the addition of 101 ml. of 0.1 N ceric cerium, we find that

$$\frac{[\mathrm{Ce}^{++++}]}{[\mathrm{Ce}^{+++}]} = \frac{1}{100} \quad \text{and}$$

$$E = 1.45 + 0.060 \log \frac{[\mathrm{Ce}^{++++}]}{[\mathrm{Ce}^{+++}]} = 1.45 - 0.12 = 1.33.$$

The change in the oxidation potential during the titration of ferrous iron with ceric sulfate is given in the table on page 489; the data have been calculated according to the method described above. The change is plotted in Figure 84.

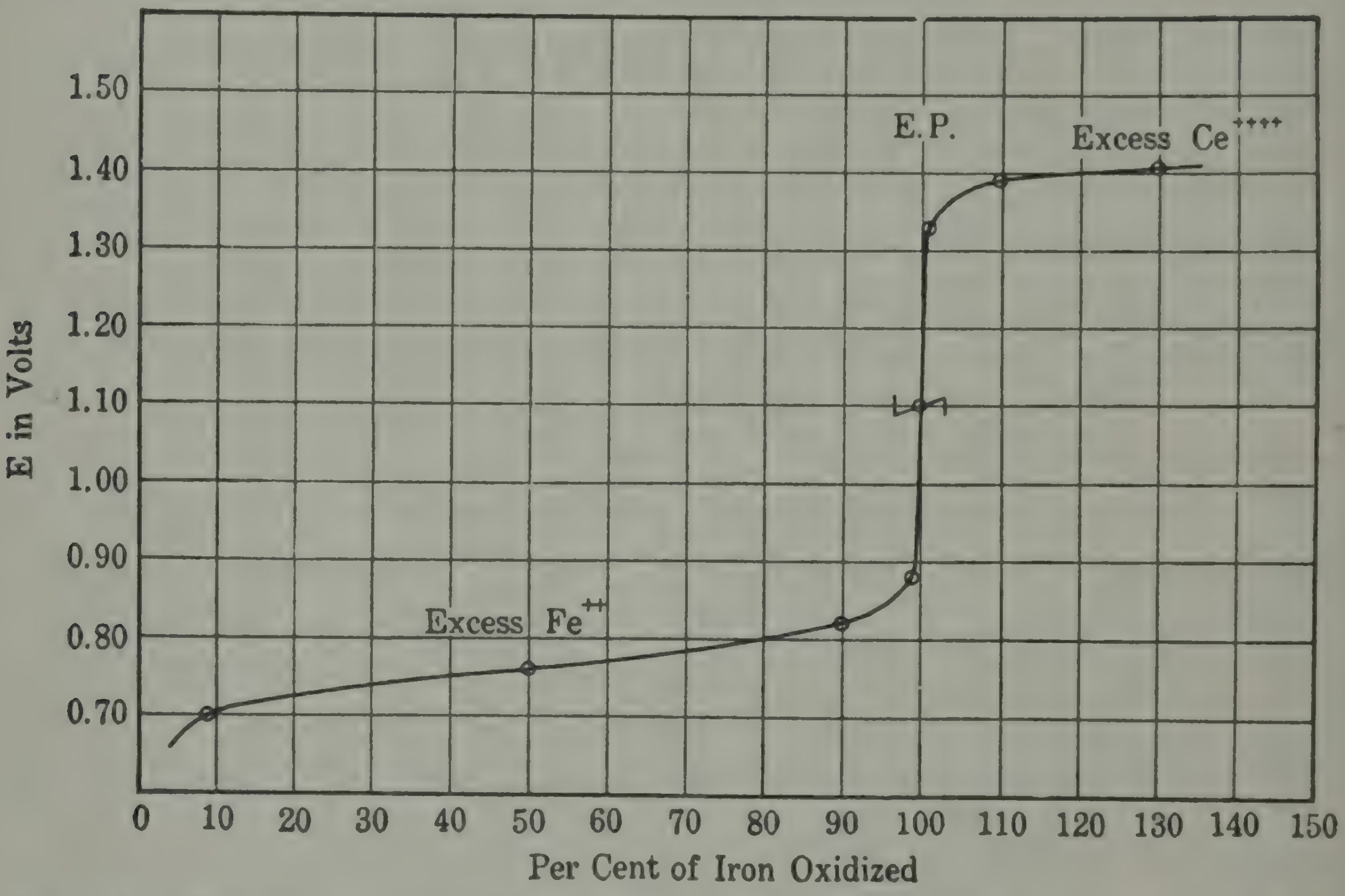


FIG. 84. Change in potential in titration of 0.1 N ferrous iron with 0.1 N ceric sulfate.

It is also a simple matter to calculate the concentration of the various components of the system during the course of the titration. This knowledge may be of importance in the application of specific indicators to the detection of the end point. In the above case, for example, we may calculate how the ferrous-ion concentration changes in the titration of 100 ml. of 0.1 N Fe^{++} with 0.1 N Ce^{++++}. After the addition of 99 ml. of 0.1 N Ce^{++++}, there is 1 ml. of 0.1 N Fe^{++} left in a volume of 200 ml., corresponding to a concentration of $\mathrm{Fe}^{++} = 5 \times 10^{-4}$. After the addition of 99.9 ml. $[\mathrm{Fe}^{++}] = 5 \times 10^{-5}$.

What is $[\mathrm{Fe}^{++}]$ at the equivalence point? According to equation (7),

$$\frac{[\mathrm{Fe}^{+++}]}{[\mathrm{Fe}^{++}]} \cdot \frac{[\mathrm{Ce}^{+++}]}{[\mathrm{Ce}^{++++}]} = K = 10^{11.5}. \tag{7}$$

TABLE LXV. TITRATION OF 100 ML. OF 0.1 N FERROUS IRON WITH 0.1 N CERIC CERIUM

CERIUM SOLUTION ADDED IN ML.	RATIO $\frac{[Fe^{+++}]}{[Fe^{++}]}$	E
9	0.1	$0.76 - 0.060 = 0.70$
50	1	0.76
91	10	$0.76 + 0.060 = 0.82$
99	100	$0.76 + 0.12 = 0.88$
99.9	1000	$0.76 + 0.18 = 0.94$
E. P. **100.0**		$\frac{0.76 + 1.45}{2} = 1.105$
Excess Ce^{++++}	Ratio $\frac{[Ce^{++++}]}{[Ce^{+++}]}$	
100.1	0.001	$1.45 - 0.18 = 1.27$
101	0.01	$1.45 - 0.12 = 1.33$
110	0.1	$1.45 - 0.06 = 1.39$

At the equivalence point the following relation holds (equation 8):

$$\frac{[Fe^{+++}]}{[Fe^{++}]} = \frac{[Ce^{+++}]}{[Ce^{++++}]}. \tag{10}$$

Therefore at this point it is found that

$$\left\{\frac{[Fe^{+++}]}{[Fe^{++}]}\right\}^2 = \left\{\frac{[Ce^{+++}]}{[Ce^{++++}]}\right\}^2 = 10^{11.5}$$

or

$$\frac{[Fe^{+++}]}{[Fe^{++}]} = \frac{[Ce^{+++}]}{[Ce^{++++}]} = 10^{5.75}. \tag{11}$$

In the above case $[Fe^{+++}]$ at the equivalence point is 0.05 molar (normal) and

$$[Fe^{++}] = \frac{[Fe^{+++}]}{10^{5.75}} = \frac{5 \times 10^{-2}}{5.6 \times 10^5} = \text{appr. } 10^{-7}.$$

After the addition of 0.1 ml. of cerium solution in excess (see Table LXV) the oxidation potential becomes equal to 1.27, whereas $[Fe^{+++}]$ remains virtually equal to 5×10^{-2}. As regards the ferrous-ion concentration:

$$E = E_{oFe} + 0.060 \log \frac{[Fe^{+++}]}{[Fe^{++}]}$$

$$1.27 = 0.76 + 0.06 \log \frac{5 \times 10^{-2}}{[Fe^{++}]}$$

$$[Fe^{++}] = \frac{5 \times 10^{-2}}{3.2 \times 10^8} = 1.5 \times 10^{-10}.$$

The ferrous-ion concentration therefore decreases abruptly in the neighborhood of the equivalence point; 0.1 per cent before this point $[Fe^{++}] = 5 \times 10^{-5}$; at the equivalence point it is equal to 10^{-7}, and with 0.1 per cent of excess of cerium it is 1.5×10^{-10}.

Indicators used for the detection of the end point in oxidation-reduction titrations.

The reagent may serve as its own indicator. If the reagent is strongly colored and is decolorized by the substance that is being determined — or if it is converted into slightly colored compounds — the end point is marked by the color of a slight excess of reagent. Thus, for example, in titrations with permanganate it is, as a rule, not necessary to add a special indicator, since a slight excess of permanganate can be easily detected by its pink color, even in the presence of slightly colored ions such as ferric ion or vanadate. If necessary, the excess of permanganate required for the detection of the end point can be determined in a blank and subtracted from the volume used in the titration.

Titrations with, or of, iodine can be carried out without an indicator in solutions having a concentration greater than 0.02 N. The end point is marked by the appearance, or the disappearance, of the intense yellow color of the iodine. Usually, however, a *specific indicator* for iodine is added near the end of the titration. Starch has the property of forming an adsorption compound with iodine in the presence of iodide which has an intense blue color. Solutions as dilute as 2 to 5 $\times 10^{-5}$ N in iodine still give a blue color with starch. Sometimes organic solvents are used for marking the appearance or disappearance of a trace of iodine at the end point. Iodine has an intense violet color in carbon tetrachloride and chloroform and is extracted by these solvents from aqueous medium. This test is even more delicate than the starch iodine reaction.

Ceric cerium has an intense yellow color, and the end point in titrations with it may be detected in colorless solutions without the addition of a special indicator. However, a much sharper end point is obtained if a suitable oxidation-reduction indicator (see below) is added.

Titrations with potassium dichromate without an indicator do not yield a sharp end point, since the greenish chromic ions formed obscure the yellow-orange color of the dichromate. Therefore an indicator must be used.

Specific indicators for the system titrated are seldom used. An example of their application is found in the titration of ferric iron with a strong reducing agent such as titanous chloride or chromous chloride. Thiocyanate gives a reddish color with ferric ions in acid medium; when all the iron has been reduced, the solution turns colorless. The color change is very sharp.

Before oxidation-reduction indicators were used, external indicators enjoyed some popularity. In the titration of ferrous iron with dichromate, for example, potassium ferricyanide or diphenylcarbazide was used as external indicator. The former reacts with ferrous iron to form Turnbull's blue, and the latter with dichromate to form an intensely red-colored compound. A drop of the solution being titrated is treated on a spot plate with a drop of ferricyanide or diphenylcarbazide. When the drop fails to give a coloration with the former or gives a red color with the latter, the end point is reached.

Oxidation-reduction indicators.

The application of oxidation-reduction indicators to titrations with strong oxidizing agents, such as ceric sulfate, potassium dichromate, and even permanganate, has become of great importance in recent years.

An *oxidation-reduction indicator is a substance the oxidized form of which has a color different from the reduced form.* The *oxidation and reduction of the indicator should be reversible.*

$$I_{Ox} + n\,e \rightleftarrows I_{Red}.$$

I_{Ox} is the oxidized form of the indicator, which has a color different from that of the reduced form, I_{Red}. A dilute iodine or iodide solution, for example, may be considered as an indicator for oxidation-reduction reactions. The iodide solution is oxidized by substances that have a higher oxidation potential than iodine, whereas substances with a lower oxidation potential reduce iodine to iodide. If a strong reducing agent is titrated with a strong oxidizing agent, iodine will be liberated at the end point. *In general, the action of an oxidation-reduction indicator does not depend upon the specific nature of the oxidant or reductant titrated but upon the relative positions of the oxidation potentials of the indicator and of the system titrated.*

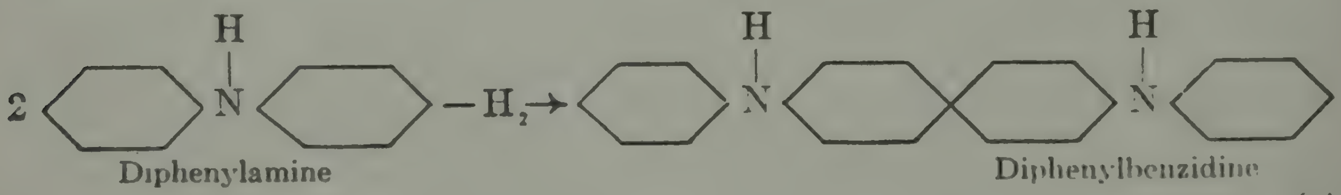
The properties of some oxidation-reduction indicators which are very useful in titrations with strong oxidizing agents such as ceric sulfate and potassium dichromate are discussed below.

The properties of oxidation-reduction indicators which change color at low oxidation potentials have been studied in great detail by Clark[1] and Michaelis.[2] They are rarely used in volumetric work and therefore are not discussed here.

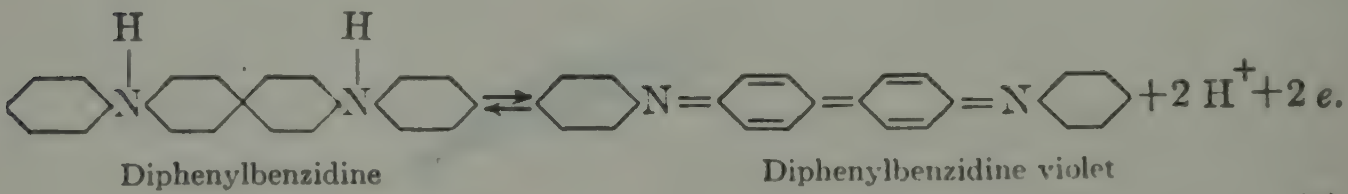
That an oxidation-reduction indicator does not react by combination with one of the constituents in the solution, but by an oxidation-reduction reaction, can be easily demonstrated by the following experiment. Add some hydrochloric acid and a few drops of diphenylamine or its sulfonic acid to a mixture of 0.01 to 0.02 *M* potassium ferricyanide and ferrocyánide. The color of the yellow solution is not changed by the addition of the indicator. In another vessel add some hydrochloric acid and indicator to a similar volume of about 0.1 *M* zinc sulfate. The solution remains colorless. However, when the zinc solution is added to the ferro-ferricyanide mixture, the beautiful violet color of the oxidation product of the indicator appears. Since zinc ferrocyanide is so much less soluble than zinc ferricyanide, the oxidation potential of the original mixture is greatly increased by the addition of the zinc and becomes large enough to permit the oxidation of the indicator.

Diphenylamine and diphenylbenzidine. Diphenylamine and diphenylbenzidine are very slightly soluble in water. Stock solutions are therefore prepared in sulfuric acid. Knop[3] was the first to propose the use of diphenylamine as an indicator in the titration of ferrous iron with potassium dichromate. Upon oxidation, diphenylamine and diphenylbenzidine give a beautiful violet oxidation product which is called diphenylbenzidine violet.

The mechanism of this oxidation can be represented by the following reactions:[4]



(1)



(2)

First, the diphenylamine is oxidized to diphenylbenzidine (equation 1); this reaction is irreversible. The oxidation of diphenylbenzidine to diphenylbenzidine violet is reversible. At an oxidation potential above + 0.76 volt (referred to the normal hydrogen electrode) the color of the system is violet; below 0.76 volt it is colorless.

---

[1] W. M. Clark, *The Determination of Hydrogen Ions*, 1928; see also Bull. 151 of the U. S. Hygienic Laboratory, *Studies in Oxidation and Reduction*; see also I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis*, Vol. I.

[2] L. Michaelis, *Oxydations-Reductions Potentiale*, 2d ed., J. Springer, Berlin, 1933.

[3] J. Knop, J. Am. Chem. Soc. *46*, 263 (1924).

[4] I. M. Kolthoff and L. A. Sarver, J. Am. Chem. Soc. *52*, 4179 (1930).

The velocity of oxidation of diphenylamine or diphenylbenzidine by dichromate in acid medium is relatively low; however, it is catalyzed by the reaction between ferrous iron and the oxidizing agent. In the application of these indicators irregular results are sometimes found. This can be caused by the very small solubility of diphenylbenzidine in water or in dilute acids. Upon oxidation of the diphenylamine, the diphenylbenzidine may precipitate, and then the latter reacts very slowly with excess potassium dichromate. If too much indicator is used, the color at the end point is sometimes found to be green; the green product formed is an extremely slightly soluble addition compound of the benzidine with the oxidized benzidine. Neither diphenylamine nor diphenylbenzidine can be used as indicators in the presence of tungstate; they form insoluble tungstates, and no color change occurs.

These indicators can be used in the titration of oxidizing agents such as permanganate, ceric cerium, dichromate, and vanadate with ferrous sulfate. In these cases the indicator shows a color change from violet to colorless. It should be realized, however, that the diphenylbenzidine violet is not stable in solutions of oxidizing agents; it is slowly and irreversibly oxidized to other organic compounds.

The slight solubilities of diphenylamine and diphenylbenzidine and their inapplicability in the presence of tungstate are a serious handicap to their general use. For this reason Sarver and Kolthoff [1] prepared a sulfonic acid of diphenylamine which is much more soluble in water and which can be used in the presence of tungstates.

Diphenylamine sulfonic acid. The barium and sodium salts of this acid are now commercially available. The stock solution is made up to contain 0.2 to 0.5 per cent of the salt in water. Upon oxidation the indicator gives a reddish-violet color resembling that of a dilute permanganate solution. The color change is brilliant and very sharp, the mechanism of the oxidation being similar to that of diphenylamine. The color change takes place at an oxidation potential of 0.83 volt, which is about 0.1 volt higher than in the case of diphenylamine.

This indicator can be used for the direct titration of oxidizing agents with ferrous sulfate, but again it should be remembered that the reddish-violet oxidation product is slowly decomposed on standing.

---

[1] L. A. Sarver and I. M. Kolthoff, J. Am. Chem. Soc. *53*, 2902 (1931).

A few drops of the 0.2 per cent indicator solution (barium salt) in a volume of 50 to 100 ml. will give sharp color changes. The indicator consumes a little oxidizing agent for its own oxidation. In titrations with 0.1 N reagents the indicator correction is so small that it can be neglected. In the titration of 0.01 N solutions the correction should be considered;[1] it corresponds to approximately 0.12 ml. of 0.01 N oxidizing agent for each 0.1 ml. of the 0.2 per cent indicator solution used. The correction can be decreased to about half of this value by using the indicator in a partly oxidized state. The red-violet oxidation product combines with unoxidized diphenylamine sulfonic acid to form a slightly soluble green addition compound of the violet and diphenylbenzidine sulfonic acid.

Willard and Young[2] recommend the following procedure for the preparation of a stock solution of the partially oxidized indicator:

100 ml. of 0.01 M diphenylamine sodium sulfonate and 5 ml. of concentrated sulfuric acid are diluted to about 300 ml. To this liquid 25 ml. of 0.1 N potassium dichromate are added slowly, followed by 8 ml. of 0.1 N ferrous sulfate. This green solution is allowed to stand for three to four days until a portion of the *supernatant* liquid gives no color when added to 100 ml. of water containing 2 ml. of 0.1 N dichromate and 5 ml. of concentrated sulfuric acid. The supernatant liquid is then siphoned off slowly, care being taken not to disturb the green precipitate. Three hundred ml. of water and 15 ml. of concentrated sulfuric acid are added to the precipitate; the latter is allowed to settle again, and the supernatant liquid is siphoned off as before. The green precipitate is then shaken up with 100 ml. of water. In a titration 0.1 ml. of the suspension gives the same color intensity as 0.2 ml. of 0.2 per cent diphenylamine barium sulfonate.

Phenanthroline-ferrous ion. The base *o*-phenanthroline, $C_{12}H_8N_2$, dissolves easily in solutions of ferrous salts, three molecules combining with one ferrous ion. The complex ferrous ions thus formed are intensely red in color; with strong oxidizing agents the ferric complex is formed, which has a blue color, the intensity of which is much less than that of the ferrous complex. Therefore in working with small amounts of indicator, the latter behaves virtually as a one-color indicator. Its properties have been studied by Walden, Hammet, and Chapman.[3] The complex ferrous ions are slowly decomposed by strong acids, or by salts of other metals (Co^{++}, Cu^{++}, Ni^{++}, Zn^{++}, Cd^{++}) which form stable complexes with the base. The ferrous iron complex does not form, or forms only very slowly, when ferrous ion is added to a strongly acid solution of the base. The blue oxidized form is remarkably resistant to further action of strong oxidizing agents. The color change red to blue is reversible:

---

[1] L. A. Sarver and I. M. Kolthoff, J. Am. Chem. Soc. *53*, 2906 (1931).

[2] H. H. Willard and Ph. Young, Ind. Eng. Chem., Anal. Ed. *5*, 154 (1933).

[3] G. H. Walden, L. P. Hammet, and R. P. Chapman, J. Am. Chem. Soc. *55* 2649 (1933).

$$\underset{(red)}{Fe(C_{12}H_8N_2)_3^{++}} \rightleftharpoons \underset{(pale\ blue)}{Fe(C_{12}H_8N_2)_3^{+++}} + e.$$

The point of visible color change (red to colorless) corresponds to 90 per cent oxidation of the indicator when one drop of a solution of the latter of the concentration given below is present. This color change occurs at a potential of 1.11 volts,[1] and hence at a much higher potential than that of the diphenylbenzidine indicators. The indicator is very useful in titrations with ceric sulfate (for example, of ferrous iron, ferrocyanide, and vanadyl ions). In titrations with potassium dichromate the diphenylamine sulfonic acid, however, is much to be preferred.

A 0.025 *M* solution of phenanthroline-ferrous sulfate is a convenient one for indicator purposes. It is prepared by dissolving the stoichiometric amount of phenanthroline monohydrate (which is commercially available) in a 0.025 *M* solution of ferrous sulfate in water. One drop of this solution is used in a volume up to 300 ml. One drop is equivalent to less than 0.01 ml. of 0.1 *N* oxidizing agent; the indicator blank is therefore negligibly small with standard solutions of this concentration and needs to be determined only when more dilute solutions are used. The stock solution can be kept unchanged for at least one year.

Erioglaucine A and Eriogreen B.[2] Erioglaucine is used in the form of a 0.1 per cent solution in water, in which it has a blue color. In strongly acid medium it is yellow, and in 0.3 to 0.4 *N* acid it has a green color. Upon the addition of a trace of permanganate or ceric sulfate, the color changes from greenish to bluish red. Eriogreen (0.1 per cent solution in water) in 0.3 to 0.5 *N* acid solution has a bluish-green color, which is changed to orange-yellow by a trace of permanganate or ceric sulfate. The color change occurs at an oxidation potential of 0.71 volt for erioglaucine and of 0.72 for eriogreen. The indicator blank is negligibly small. A few drops of the indicator in a volume of 200 to 400 ml. give a sharp color change with 0.1 ml. of 0.01 *N* permanganate or ceric sulfate. A disadvantage of these indicators is that the oxidized forms are rather unstable, especially in the presence of an excess of oxidizing agent; moreover the color changes become less pronounced in strongly acid media. Therefore the ferrous-phenanthroline complex is, in general, much to be preferred.

For the sake of convenience we give in the following table a selected group of oxidation-reduction indicators with their color changes and oxidation potentials in acid medium.[3]

---

[1] D. N. Hume and I. M. Kolthoff, J. Am. Chem. Soc., In press (1943).

[2] J. Knop, Z. anal. Chem. 77, 111 (1929).

[3] Oxidation potentials at pH of about zero against the normal hydrogen electrode.

Table LXVI. Selected List of Oxidation-reduction Indicators[1]

Indicator	Color Change		E_0 at pH = 0
	(Ox)	(Red)	
Indigo monosulfonate	blue	colorless	0.26
Phenosafranine	red	colorless	0.28
Indigo tetrasulfonate	blue	colorless	0.36
Methylene blue	green-blue	colorless	0.36
1-Naphthol-2-sulfonic acid indophenol	red	colorless	0.67
Diphenylamine (diphenylbenzidine)	violet	colorless	0.76 ± 0.1
Diphenylamine sulfonic acid	red-violet	colorless	0.85
Erioglaucine A	red	green	1.0
Setoglaucine	pale red	yellow-green	1.06
p-Nitrodiphenylamine	violet	colorless	1.06
o-*m*-Diphenylamino dicarbonic acid	blue-violet	colorless	1.12
o-*o*′-Diphenylamino dicarbonic acid	blue-violet	colorless	1.26
p-Ethoxychrysoidine	pale yellow	red	1.0
o-Phenanthroline ferrous complex (ferroin)	pale blue	red	1.05 (distinct color change 1.11)
Nitro-*o*-phenanthroline ferrous complex	pale blue	violet-red	1.25 (color change 1.31)
Ruthenium tridipyridyl dichloride[a]	yellow	colorless	1.33

[a] J. Steigmann, N. Birnbaum, and S. M. Edmonds, Ind. Eng. Chem., Anal. Ed. *14*, 30 (1942). The indicator gives an excellent end point in the titration at room temperature of oxalate in 2 *N* perchloric acid with ceric nitrate.

It is now a simple matter to interpret the behavior of an oxidation-reduction indicator in the titration of ferrous sulfate, for example, with a strong oxidizing agent. Ferrous-phenanthroline changes from red to almost colorless at an oxidation potential of 1.11 volts. From Table LXV (p. 489) we see that in the titration of ferrous iron with ceric sulfate the oxidation potential at the equivalence point is 1.10 volts; the indicator therefore is still present in the red form. After the addition of a 0.1 per cent excess of ceric sulfate the potential changes to 1.27 volts, and the indicator is oxidized. Evidently the titration error is negligibly small.

Diphenylamine sulfonic acid is oxidized to the violet form at an oxidation potential of 0.83 volt, which is a little before the end point. In order to get good results with this indicator (and with diphenylamine and diphenylbenzidine), it is necessary to reduce the oxidation potential of the iron system, which can be done as we have seen by transforming the ferric iron into a complex by the addition of phosphoric acid or fluoride. Under those conditions excellent results are obtained in the titration of ferrous iron with dichromate or ceric sulfate, using the diphenylamine or diphenylbenzidine as indicator for the detection of the end point.

---

[1] A detailed description of the properties, preparation, and application of oxidation-reduction indicators with an oxidation potential greater than 0.7 volt is given by T. H. Whitehead and C. C. Wills, Jr., Chemical Reviews *29*, 69 (1941).

These indicators and the ferrous-phenanthroline are also very valuable in the titration of strong oxidizing agents with ferrous sulfate.

General procedures for oxidation or reduction of substances prior to titrations.

Various substances which can exist in different states of oxidation can be transformed by suitable means into a higher state of oxidation and titrated with a reducing agent, or into a lower state of oxidation and then titrated with an oxidizing agent. In all these cases the substance used for the oxidation or reduction must generally be absent when the titration is made.

Sodium bismuthate is a powerful oxidizing agent; it oxidizes manganous manganese to permanganate at room temperature in nitric acid solution. After the oxidation is complete the excess is easily removed by filtration, because the bismuthate is insoluble.

Lead dioxide in acid medium also can be used in several cases for oxidation purposes.

Potassium persulfate, $K_2S_2O_8$, is often used as an oxidizing agent, usually in combination with a little silver salt which acts as a catalyst. Manganese, for example, is quantitatively oxidized to permanganate if the oxidation is carried out in the presence of phosphoric or hydrofluoric acid; trivalent chromium is oxidized to dichromate, and vanadyl to vanadate. The excess of persulfate can be decomposed by boiling:

$$K_2S_2O_8 + H_2O \rightarrow 2\ KHSO_4 + \tfrac{1}{2}\ O_2.$$

Hydrogen peroxide is often used as an oxidizing agent in alkaline medium: it is decomposed by boiling the alkaline solution. This decomposition is catalyzed by the addition of a little nickel salt or more strongly by iodide.

Recently Willard and Merritt[1] introduced ozone as an oxidizing agent. The oxidation potential of the system

$$O_3\ (g) + 2\ H^+ + 2\ e \rightarrow O_2\ (g) + H_2O$$

is 2.07 volts. Hence ozone is a powerful oxidizing agent. The excess of ozone and the oxygen formed are readily removed after the oxidation by passing an inert gas through the solution. Manganese in 1 to 2 *M* perchloric acid solution and in the presence of silver (nitrate) as a catalyst is quantitatively oxidized to permanganate. The latter can be titrated by standard procedures. Trivalent cerium is quantitatively oxidized to the quadrivalent form in a solution containing phosphoric and sulfuric acid. Ceric phosphate separates in the form of a white gel which is dissolved by sulfuric acid. Vanadyl ion is quantitatively oxidized to vanadate. Chromic ion in acid medium is scarcely oxidized unless silver nitrate is present as a catalyst and even then only in small amounts. Selenite and tellurite are quantitatively oxidized to selenate and tellurate in alkaline solution, but there is only slight oxidation in acid medium. Trivalent arsenic and antimony are completely oxidized in acid or alkaline solution. Mercurous perchlorate is readily oxidized to the mercuric form. Cobaltous and nickelous hydroxides form the corresponding trivalent hydroxides. Nitrite is oxidized to nitrate, hypophosphite and phosphite are oxidized to phosphate. Iodide is quantitatively oxidized to periodate in 1 to 10 per cent sodium hydroxide solution. Chloride can be present in any amount, but bromide interferes.

---

[1] H. H. Willard and L. J. Merritt, Jr., Ind. Eng. Chem., Anal. Ed. *14*, 486 (1942).

For reducing purposes, metals, metal amalgams, and stannous chloride are often used, more rarely hydrogen sulfide and sulfur dioxide. The excess of the latter two can be easily removed by boiling, but they are usually slow in their reducing action. Stannous chloride, which is a powerful reducing agent (see Table LXIV), is of special importance in the determination of iron.

Metals are powerful reducing agents (compare their normal potentials [Table XXVIII, p. 146] with those of oxidizing and reducing substances [Table LXIV, p. 483]). The metals which are above hydrogen in the electromotive series, such as zinc or cadmium, discharge hydrogen ions in acid medium:

$$Zn + 2\,H^+ \rightarrow Zn^{++} + H_2.$$

Therefore their application to reductions is limited by the hydrogen potential. However, in Chapter X we saw that hydrogen has a very high overvoltage on mercury; therefore if the metals are used in the form of amalgams, it is possible to prevent hydrogen formation. Such metal amalgams are powerful reducing agents and can be used for the reduction of vanadate (V^{V}) to V^{IV}, V^{III}, and V^{II}; of molybdate (Mo^{VI}) to Mo^{III}; of tungstate (W^{VI}) to W^{V} or to W^{III}; of uranyl (U^{VI}) to U^{IV} and U^{III}; of Ti^{IV} to Ti^{III}; of Cr^{III} to Cr^{II}, etc. By the use of various amalgams differential reductions can be made; for details the student is referred to I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis*, Vol. II.

A popular amalgam is that of zinc, which is used in the form of a filtering column (Jones reductor) or an amalgamated zinc spiral (see procedure on p. 598).

Induced reactions.

Various reducing agents, such as trivalent arsenic and antimony, hydrogen peroxide, or stannous tin can be titrated accurately with permanganate in the presence of hydrochloric acid. This is to be expected, because the substance to be titrated is much more easily oxidized than the chloride. Therefore oxidation of the latter, which moreover takes place slowly, does not occur until the substance titrated has been quantitatively oxidized. This behavior, however, is not observed in the titration of ferrous iron with permanganate. A small part of the chloride is oxidized to chlorine or hypochlorous acid, HClO, during the titration of the ferrous iron; and since the chlorine reacts only slowly with the ferrous iron, too much oxidizing agent will be used up. The reaction between ferrous iron and permanganate *induces* the reaction between hydrochloric acid and permanganate, and we encounter here a so-called *induced reaction.* The explanation is that the ferrous iron is first oxidized to a higher state of oxidation than ferric iron; this higher oxidation form of iron is not stable and reacts practically instantaneously with the ferrous ions to form ferric iron. However, in the presence of hydrochloric acid part of the higher oxidation form of the iron reacts with chloride, thus giving rise to the formation of a little chlorine. This induced reaction can be prevented by the addition of a manganous salt. In cases where iron is to be titrated with permanganate in the presence of hydrochloric acid, the manganous salt is added as Zimmermann-Reinhard solution, which is a solution of manganous sulfate in dilute sulfuric and phosphoric acids (see p. 601). The action of the manganese may be explained by assuming that it reacts with the higher oxidation form of iron with the formation of tri- or quadrivalent manganese, which in turn reacts instantaneously with ferrous sulfate. The oxidation of chloride is thereby prevented or reduced.

Titrations of ferrous iron with dichromate and ceric sulfate can be made without difficulty in the presence of chloride if the concentration of the latter is less than 1 N.

In all oxidations of ferrous iron there is intermediately produced a form of iron which has a stronger oxidizing action than the ferric iron. The oxidation of diphenylamine, diphenylbenzidine, and diphenylamine sulfonic acid by dichromate to the violet oxidation products is relatively slow; however, it is strongly induced (or catalyzed) by the reaction between ferrous iron and the oxidizing agent. If one adds a few drops of the above indicator solutions to a dilute acid dichromate solution, the color of the solution does not change instantaneously. The brilliant violet color develops immediately upon the addition of a trace of ferrous iron.

The exact mechanism of induced reactions is not well understood at present, and our knowledge of them is still more or less empirical.[1] In any oxidation-reduction reaction one must take into account the possibility of the occurrence of an induced reaction. Under ordinary conditions titrations are carried out in the presence of air, and hence of oxygen. Although various reducing agents are only slowly oxidized by air, this reaction may be induced during the titration of the reducing agent with the oxidizing substance. Iodide, for example, is slowly oxidized by air in acid medium; various reactions, however, may induce the air-oxidation of iodide. This, for example, takes place in the iodometric determination of vanadate. The acid solution of vanadate is treated with an excess of iodide, and the liberated iodine is titrated with sodium thiosulfate. The reaction between vanadate and iodide induces the air-oxidation of the latter, and high results are found.[1] In such cases good results can be obtained by making the titration in an atmosphere of carbon dioxide or other inert gas.

---

[1] For a more detailed discussion see I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis*, Vol. I (1942); and I. M. Kolthoff and R. S. Livingston, Ind. Eng. Chem., Anal. Ed. 7, 209 (1935).

PROBLEMS[2]

1. Calculate the oxidation potential of a mixture of potassium ferrocyanide and ferricyanide in which the ratio of the two is 100 : 1; 10 : 1; 1 : 1; 1 : 10; 1 : 100. Do the same for a mixture of stannous tin with stannic tin. The normal potential of the ferro-ferricyanide system is 0.44 volt, that of the stannous-stannic tin, 0.2 volt.

2. The normal potential of the vanadate-vanadyl system,

$$VO_4^{\equiv} + 6\,H^+ + e \rightleftarrows VO^{++} + 3\,H_2O,$$

at $[H^+] = 1$ is equal to 1.2 volts. What is the oxidation potential at 30° and at pH = 1, and $[VO_4^{\equiv}] = [VO^{++}]$? *Ans.* 0.84 volt.

3. What is the equivalent weight of vanadate in the titration with ferrous iron? Balance the equation and write the two partial reactions.

4. The normal potential of the $VO_4^{\equiv} \rightarrow VO^{++}$ system is 1.2; that of $VO^{++} \rightarrow V^{+++}$ is 0.4. Is it possible to reduce $VO_4^{\equiv}$ to VO^{++} and V^{+++} respectively with ferrous sulfate or with titanous chloride? (Normal potential $Fe^{+++} \rightarrow Fe^{++}$ is 0.76. Normal potential $Ti^{++++} \rightarrow Ti^{+++}$ is -0.04.)

5. What is the equivalent weight of stannous chloride in the titration with ferric sulfate? Is this reaction quantitative at the equivalence point? Can phenanthroline-ferrous complex be used as an indicator? (Normal potential $Sn^{++++} \rightarrow Sn^{++}$ is 0.2, $Fe^{+++} \rightarrow Fe^{++}$ is 0.76.) The indicator changes from red to almost colorless at a potential of 1.1 volt.

What should be the oxidation potential of a useful indicator in this titration?

---

[1] G. Edgar, J. Am. Chem. Soc. *38*, 2369 (1916); W. C. Bray and J. B. Ramsey, J. Am. Chem. Soc. *55*, 2279 (1933).

[2] The problems presented are of an advanced nature and need not be given in a beginning course.

CHAPTER XXXII

PHYSICO-CHEMICAL DETERMINATION OF THE END POINT. ELECTROMETRIC TITRATIONS

Most often the end point of a titration is found in a visual way with the aid of a suitable indicator. There are, however, various cases in which this ordinary method cannot well be applied. In many instances no suitable indicator is available for the direct determination of the end point, especially in precipitation reactions, such as in the direct titration of calcium with oxalate (or the reverse) or of barium with sulfate (or the reverse). In other cases the color change at the end point may be too vague to allow the application of the visual method to accurate work. In addition, the solution to be analyzed may be colored, thus interfering with the detection of the color change of the indicator. If the maximum in the absorption spectrum of the indicator form present at the end point lies at a wave length distinctly different from that of the colored material present in the original solution, the end point can still be perceived with the aid of a simple hand spectroscope. One adds standard solution until the absorption band of the colored form of the indicator suddenly appears. For acidimetry and alkalimetry various fluorescent indicators are available, one form of which is not fluorescent, whereas the other form (ion or undissociated molecule) is. In such cases the end point can be recognized by the sudden appearance or disappearance of a fluorescence in the solution. However, the last two types of methods are seldom applied since they detract materially from the simplicity of ordinary volumetric methods and cannot boast a high degree of precision.

In those cases in which the ordinary method fails to give useful results for the reasons mentioned, one may often resort to a physico-chemical determination of the end point. Quite generally some physico-chemical property of a solution changes more or less abruptly when the end point is reached or passed. For the sake of illustration, we give the following example, which, however, is of no practical significance. Let us titrate a solution of 0.1 N hydrochloric acid with a strong standard sodium hydroxide solution and assume that the volume of the solution does not change during the titration. Let the freezing point of the solution be the physico-chemical property which is used for the detection of the end point. During the titration the acid is transformed into sodium chloride; and since the volume does not change, we have a 0.1 N sodium chloride solution at the equivalence point. Since 0.1 N hydrochloric acid and 0.1 N sodium chloride produce virtually the same freezing-point lowering, the freezing point will remain unaltered until the end point is reached. Further addition of sodium hydroxide increases the total concentration of strong electrolyte in the solution, and the freezing point is correspondingly depressed. Therefore, if one would measure the freezing point of the solution after successive additions of reagent and plot the values obtained against the amount of reagent, two straight lines intersecting at the equivalence point would be obtained, as illustrated in Figure 85.

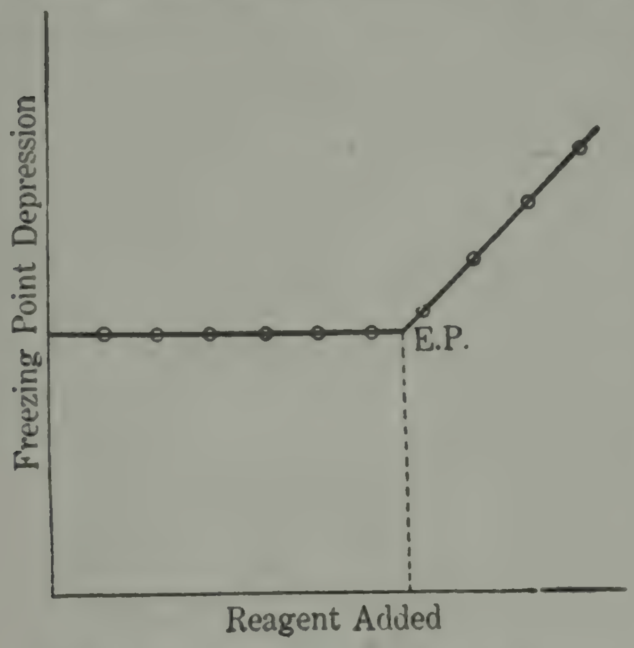


FIG. 85. Theoretical cryoscopic titration curve of hydrochloric acid with sodium hydroxide (or reverse).

Thus we have developed a *cryoscopic* method for the determination of the end point. Naturally, no one would ever apply this method in practical analysis, since the measurement of the freezing-point depression is not a very simple matter. In a similar way one could measure the change of other physico-chemical properties of the solution during the titration. If the change in the density of the solution were determined, lines comparable to those given in Figure 85 would be found, and we would have a *densimetric* method for the determination of the end point. If the change of the refractive index were determined with a refractometer or interferometer, a *refractometric* method would be used. Use could also be made of the heat of reaction during the titration by plotting the values found against the amount of reagent added (*calorimetric method*). In certain cases an indicator could be added to the system, a physico-chemical property of which undergoes a sudden change at the end point. The higher homologues of the fatty acids are weak acids, slightly soluble in water and strongly capillary active (they decrease the surface tension of the solution markedly). The alkali salts of these acids have hardly any effect upon the surface tension of the water. Therefore if one were to titrate an acid in the presence of such a capillary-active indicator and measure the surface tension of the solution (for example with a stalagmometer), a sudden change in the surface tension would indicate the location of the end point (*surface tension method*). Various emulsoids, such as the proteins, have, when dissolved in water, a viscosity which has a pronounced maximum at a certain pH (isoelectric point). Therefore if the viscosity were measured during the addition of reagent, such emulsoids could be used for titrations to a certain pH (*viscosimetric* method). None of the above-mentioned methods has practical significance, and it is beyond the scope of this book to develop in detail the theories underlying them.

Differing from the above methods are the so-called *electrometric* titrations, which are of great practical value. Electrometric titration methods can be classified into (1) *potentiometric*, (2) *conductometric*, and (3) *amperometric*, the principles of which are entirely different.

Potentiometric titrations.

The theory of potentiometric titrations resembles very closely that of ordinary titrations. In the following, the principles and practical applications are briefly discussed. The student is referred to special texts[1] for details.

Theory of potentiometric titrations. In the chapter on electroanalysis (p. 140) it was mentioned that a potential difference exists between a metal and a solution containing ions of the same metal. This potential difference, usually denoted as the potential (E), is given by the Nernst equation:

$$E = -\frac{RT}{nF} ln \frac{K}{[M^{n+}]} \tag{1}$$

in which n denotes the valence of the metal ions, K a constant, and $[M^{n+}]$ the metal-ion concentration (or better the activity). This expression can be written in the following form for 25°:

$$E = -\frac{0.0591}{n} \log_{10} \frac{K}{[M^{n+}]}$$

or since K, is a constant,

$$E = E_o + \frac{0.0591}{n} \log [M^{n+}]. \tag{2}$$

If $[M^{n+}]$ becomes equal to 1, we find that $E = E_o$. Therefore E_o represents the potential of the electrode at a metal-ion concentration (strictly activity) of unity as measured against the normal hydrogen electrode. Let us now assume that the potential of an electrode can be measured in some simple way. From equation (2) we see that the following relation exists between the potential and the metal-ion exponent pM^{n+}:

$$E = E_o - \frac{0.0591}{n} \text{p}M^{n+}. \tag{3}$$

When dealing with the silver electrode, this expression becomes:

$$E = E_{o_{\text{Ag}}} - 0.0591 \text{ pAg}$$

and when dealing with a hydrogen electrode:

$$E = E_{o_{\text{H}}} - 0.0591 \text{ pH}.$$

If we change the silver- or hydrogen-ion concentration of the solution ten times (or the ion exponent by 1), the change in the potential of the corresponding electrodes is equal to 0.0591 volt. Therefore there is a simple relation between the potential of the electrode and the corresponding ion exponent of the solution.

In Chapters XXIX and XXX we derived the change of the ion exponent in acidimetric, alkalimetric, and precipitation titrations. It was shown there that a very sudden change in the value of the ion exponent occurs at the equivalence point. In ordinary titrations this abrupt change is marked by a sharp color change of a suitable indicator. It is now evident that instead of using an indicator for detecting the end point, we can employ an electrode which responds to a change in the ion concentration of the solution during the titration and measure its potential after successive additions of reagent. An abrupt change of the potential indicates the location of the equivalence point. It is easy to see that the titration curve (for example, that of 0.1 *N* hydrochloric acid with 0.1 *N* sodium hydroxide, Fig. 79 and p. 454) is identical with the curve showing the change in the potential of the hydrogen electrode during the titration, if we plot the potential instead of pH and take our units such that the length of one unit in the pH on the ordinate corresponds to 0.0591 volt.

---

[1] I. M. Kolthoff and N. H. Furman, *Potentiometric Titrations*, 2d ed., John Wiley and Sons, New York, 1931; Erich Müller, *Elektrometrische (Potentiometrische) Massanalyse*, 5 Auflage, Theodor Steinkopff, Dresden, 1932; I. M. Kolthoff and H. A. Laitinen, *The Determination of pH. Electrometric Titrations*, 2d ed., John Wiley and Sons, New York, 1941.

Therefore the hydrogen electrode serves as an *indicator electrode* in the detection of the *end point*. The hydrogen electrode (or one of its substitutes) may be quite generally employed in acidimetry and alkalimetry. Instead of the hydrogen electrode itself, other electrodes are available, the potentials of which change with the pH in the same manner as that of the hydrogen electrode. In this connection the quinhydrone, antimony, air (oxygen), and especially the glass electrodes [1] may be mentioned. All of these have certain limitations, which are discussed in detail in the works referred to above.

For titrations in which silver ions are involved (titrations of, or with, silver solutions; e.g., halides, cyanides, etc.), a silver electrode is used; for titrations of, or with, mercurous ions, a mercury electrode, etc.

Metals which are above, or just below, hydrogen in the electromotive series (Table XXVIII, p. 146) cannot be used as indicator electrodes, since they are too easily polarized.

Potentiometric titrations are extremely useful in oxidation-reduction reactions, especially in those cases in which systems of different oxidation-reduction potentials are present. In such cases it is often possible to determine the individual amounts of various oxidizing or reducing substances in one titration.

In the measurement of oxidation-reduction potentials, a straight wire, spiral, foil, or, still better, a gauze of a noble metal — as a rule bright platinum — serves as the indicator electrode.

The change in the oxidation potential during a titration has been discussed at length in Chapter XXXI. An illustration of the change in the potential in the titration of ferrous iron with ceric sulfate is given in Figure 84 (p. 488). It is seen that a large break in the potential indicates the location of the equivalence point. Potentiometric titrations are advantageously applied in those cases in which several constituents with different oxidation potentials react with the same reagent. The first break in potential indicates the complete reduction of the strongest oxidizing agent, the second one that of the second, etc. Suppose, for example, that a mixture containing dichromate, ferric iron, and cupric copper is to be analyzed. By one titration with titanous chloride or chromous chloride it is possible to determine each of the three constituents

---

[1] See M. Dole, *The Glass Electrode*, John Wiley and Sons, New York 1941.

First the dichromate is reduced, point *A* in Figure 86 corresponding to the amount of reducing agent equivalent to the dichromate content; the amount of reagent added between *A* and *B* corresponds to the iron content, and that between *B* and *C* to the copper content.

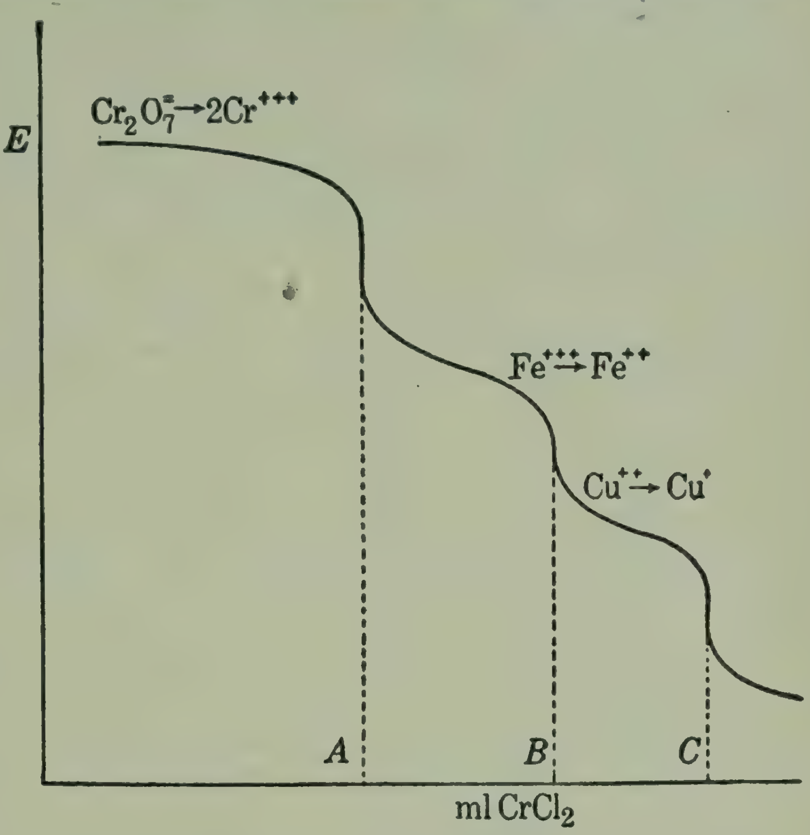


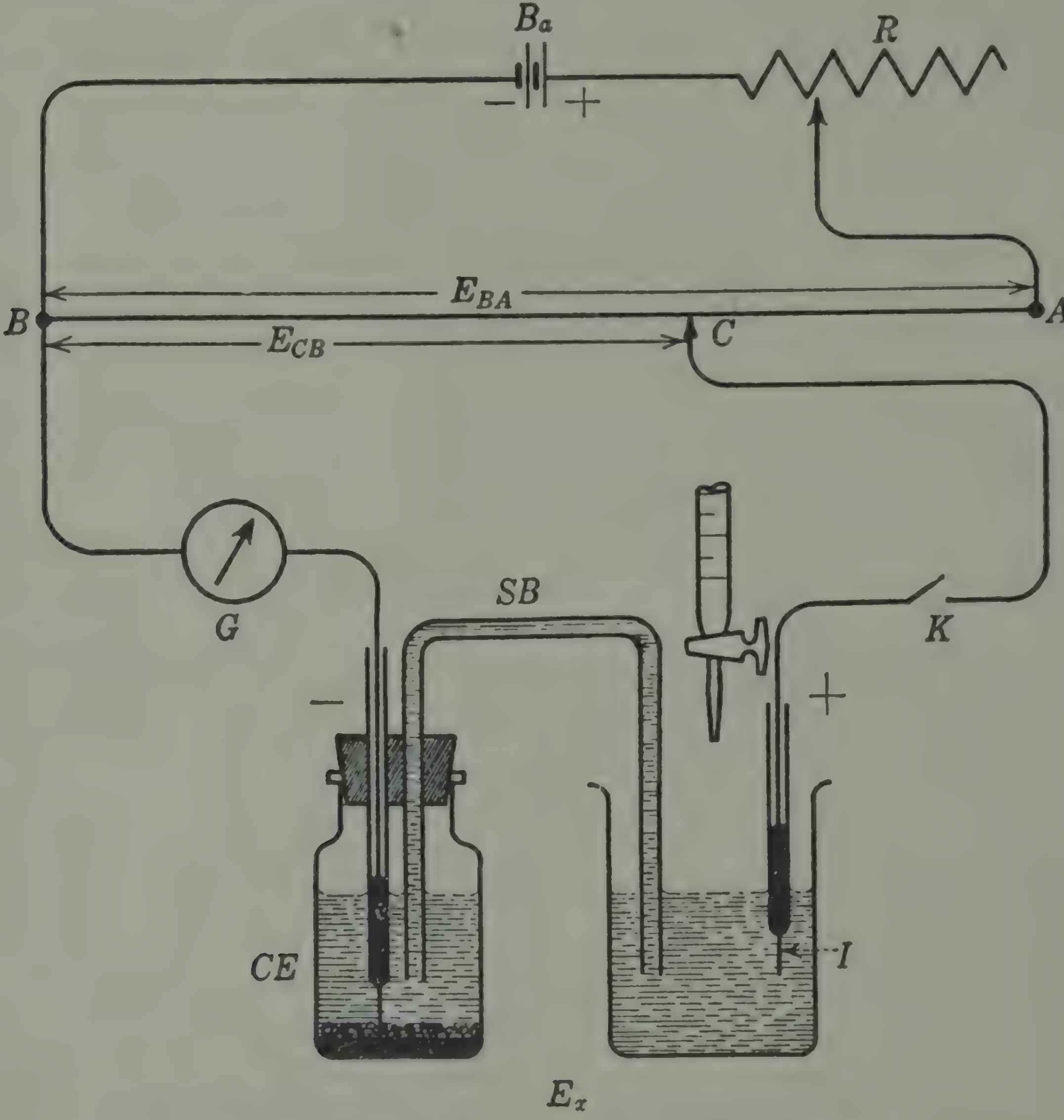
FIG. 86. Successive titration of dichromate, ferric iron, and cupric copper with chromous chloride.

Performance of a potentiometric titration. Only the principle of the performance of a potentiometric titration is discussed here; for different methods and practical details the student must be referred to special monographs.

It is impossible to measure a single potential difference between an electrode and a solution. In potentiometric measurements, however, we are not interested in the absolute potentials of the electrodes but in the changes of the potential during the titration. These can be found in a simple way by making electrolytic contact between the indicator electrode in the unknown solution (a half-cell) and some standard reference electrode (also a half-cell). In this way we build up a galvanic cell, the E.M.F. of which can be measured simply and accurately In most practical work we use some type of "calomel" electrode as a standard reference electrode or, as it is called, a standard half-cell. Its potential is constant and does not vary during the titration. Therefore the change in the E.M.F. during the titration is due solely to the change in potential of the indicator electrode. The calomel electrode (see Fig. 87) is a mercury-mercurous ion electrode. The mercury is in equilibrium with a potassium chloride solution of a certain concentration which is saturated with mercurous chloride (calomel). A platinum wire sealed into the end of a glass tube makes electrical contact between the mercury and the outside circuit. Electrolytic contact between the potassium chloride solution in the calomel half-cell and the liquid in the titration cell is usually made by a "salt bridge." This is a narrow U-shaped tube filled with a jelly of 3 per cent agar in saturated potassium chloride solution.

The simplest way to measure the E.M.F. of a cell is to connect the terminals (here the two electrodes) with a voltmeter and read the voltage directly. This method, however, does not yield exact results, since a measurable current must be drawn from the cell, thus causing reactions at the electrodes and changes in the concentrations of the ions which determine the potentials of both electrodes; in other words, *polarization* results.

Therefore, in the exact measurement of the E.M.F., one prevents polarization by balancing the unknown E.M.F. with an opposing known E.M.F. (the value of which can be easily changed), and thus practically no current is drawn from the cell. If the unknown and opposing E.M.F. are exactly equal, no current will flow through the circuit, as indicated by no deflection of the galvanometer (*G* in Fig. 87), which serves as a nullpoint instrument. The method on which this measurement is based is called the compensation method of Poggendorff-DuBois-Raymond.



Ba, battery (2 volts)
R, variable resistance
AB, slide wire
C, sliding contact
G, galvanometer
K, tapping key
SB, salt bridge
CE, calomel electrode
I, Indicator electrode

FIG. 87. Apparatus for potentiometric titration.

Ba is a battery, furnishing the opposing E.M.F.; a lead storage battery or two dry cells is suitable for the purpose. The battery is connected to the terminals of the slide wire *AB* by thick copper wires of negligible resistance. The slide wire consists of a thin resistance wire of uniform cross section. The sliding contact *C* can be moved between *A* and *B* over a scale which is divided into 1000 equal parts. The positive electrode of the unknown cell (in Fig. 87 the indicator electrode) is connected to the sliding contact *C*, and the negative electrode with point *B*, the zero point on the slide wire. It is evident that the "unknown" cell sends a current through the circuit in a direction opposite to that furnished by the battery.

By moving the sliding contact C between A and B, a point will be found at which no current flows through the circuit, as indicated by no deflection of the galvanometer G. When this point is reached, the E.M.F. (E_x) of the unknown cell is equal to the E.M.F. between C and B (E_{CB}).

The E.M.F. between A and B is equal to the E.M.F. of the battery (E_{BA}). Since the slide wire has a uniform resistance, it is evident that there is a uniform drop of the E.M.F. over the entire length of the wire.

Therefore, if BC represents the length on the slide wire when the system is balanced, it follows from Ohm's law that:

$$E_{CB} = i\,R_{CB}$$

$$E_{BA} = i\,R_{BA}$$

$$E_x = E_{CB} = \frac{R_{CB}}{R_{BA}} E_{BA} = \frac{CB}{1000} E_{BA}.$$

If $E_{BA} = 2$ volts and the sliding contact C is exactly at 500, then

$$E_x = \frac{500}{1000} \times 2 = 1 \text{ volt}.$$

E_{AB} can be adjusted to exactly 2.000 volts by means of the rheostat R. In order to do this, the unknown element in the circuit CE_xGB is replaced by a "normal element" or standard cell, the E.M.F. of which is exactly known. The Weston standard cell, which is generally used for this purpose, has an E.M.F. of 1.0183 volts at 20°.

Therefore E_x is now known, and we find that

$$E_x = 1.0183 = \frac{BC}{1000} E_{BA}. \tag{4}$$

If we wish to adjust E_{BA} to exactly 2 volts, it is evident that the sliding contact C must be fixed at a point where the length of BC is

$$BC = \frac{1018.3}{2.0000} = 509.1.$$

During the adjustment of E_{BA}, C is fixed at 509.1, and the resistance of the rheostat R is adjusted until the system is balanced. In all further measurements of E_x, the resistance of R is kept unchanged, and we find

$$E_x = \frac{BC}{1000} \times 2.000 \text{ volts}.$$

The reading of BC is multiplied by 0.002 in order to find E_x in volts when the system is balanced. If E_{BA} were adjusted to 1.000 volt, the reading BC divided by 1000 would give the value of E_x. This is the principle upon which the *potentiometer* is based. In potentiometric titrations we are not interested in the absolute values of E_x but in the changes of E_x, especially just before and just after the equivalence point.

Therefore if we keep E_{BA} constant during the titration, the change of BC is directly proportional to the change of E_x (equation 4), and it suffices to use the readings of BC as indications of the change in the potential.

As an example of a potentiometric titration we may consider the titration of 50 ml. of 0.000161 N silver nitrate solution with 0.00100 N potassium iodide solution. A platinum-gauze electrode electrolytically coated

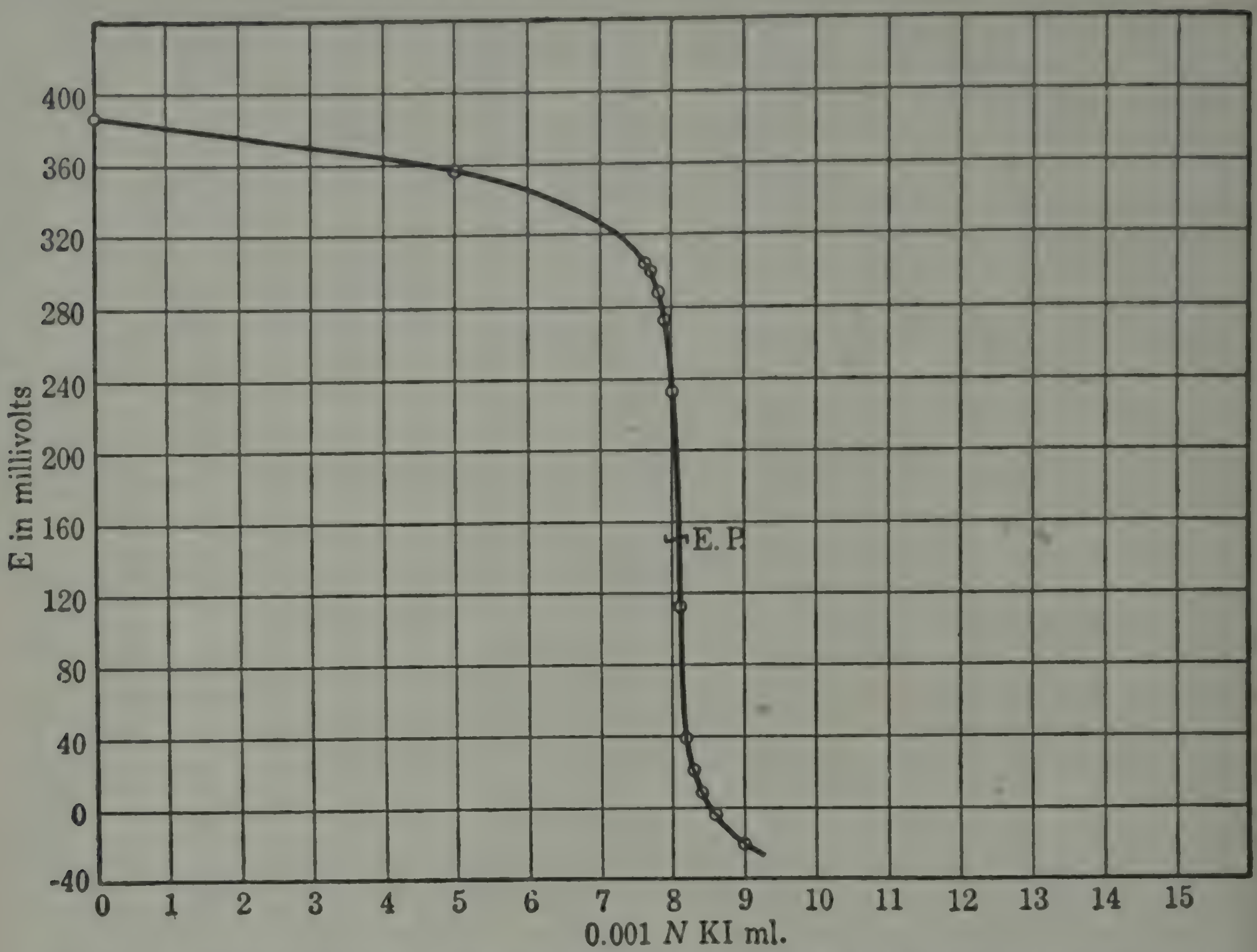


FIG. 88. Potentiometric titration of 50 ml. of 0.000161 *N* silver nitrate solution with 0.00100 *N* potassium iodide.

with a thin layer of silver was used as indicator electrode, and a saturated calomel electrode (saturated with potassium chloride) served as a reference half-cell. The data found are given in Table LXVII and plotted in Figure 88.

TABLE LXVII. POTENTIOMETRIC TITRATION OF 50 ML. OF 0.000161 *N* SILVER NITRATE SOLUTION WITH 0.00100 *N* POTASSIUM IODIDE SOLUTION

KI ADDED ML.	E_x	$\frac{\Delta E}{\Delta c}$
0	+ 0.387 *	
5.0	0.356	
7.6	0.305	6
7.7	0.299	12
7.8	0.287	14
7.9	0.273	41
8.0	0.232	120
8.1	0.112	74
8.2	0.038	19
8.3	0.019	12
8.4	+ 0.007	
8.6	− 0.003	
9.0	− 0.021	

* + indicates that the silver electrode was positive against the saturated calomel electrode; − denotes the reverse.

From the curve it can be found that the inflection point occurs after the addition of 8.05 ml. of iodide, and this then indicates the end point. However, it is not necessary to plot the data in order to find the location of the end point. In the theoretical discussion of titration curves (Chapter XXIX) it was pointed out that the greatest change in the potential, on adding equal increments of reagent, occurs at the equivalence point. Therefore if we calculate the change of E_x produced by the addition of equal increments of reagent, a maximum will be found at the equivalence point. These changes for the example given are recorded in the third column of Table LXVII under the heading $\frac{\Delta E}{\Delta c}$. $\frac{\Delta E}{\Delta c}$ is the change of the potential in millivolts caused by 0.1 ml. increments of reagent. It is apparent that $\frac{\Delta E}{\Delta c}$ reaches a maximum after the addition of 8.06 ml. of iodide. The normality of the silver solution titrated is accordingly found to be 0.0001612.

Even at these high dilutions the potentiometric method yields highly precise and accurate results in this case. It is also seen that the equivalence point is reached when E_x has become equal to 0.150 volt. Therefore we could simplify the performance of the titration by placing the sliding contact C at the point corresponding to 0.150 volt and slowly adding reagent until no current flows in the circuit. Before this point is reached, the galvanometer will deflect to one side; at the equivalence point the needle will not move; and when this point is passed, the needle swings to the other side.

Conductometric titrations.[1]

In conductometric titrations the electrical conductivity of the solution is measured after successive additions of reagent, and the values found are plotted against the volume of reagent added. As a rule two straight lines are obtained which intersect at the equivalence point. In contrast to potentiometric titrations, in which the electrode used is specific for the system titrated, we find that in conductometric titrations all ions present contribute to the electrical conductivity of the solution.

If an electrolyte is added to a solution of another electrolyte without changing the volume to any appreciable extent, the conductivity increases in so far as the electrolytes do not react with each other. If an ion of one electrolyte unites with an ion of the other to form a slightly dissociated or slightly soluble substance or if it changes the total ion concentration by an oxidation or reduction process, then the conductivity of the solution may change in three different ways, before the equivalence point has been reached:

---

[1] A more detailed account of conductometric titrations may be found in I. M. Kolthoff, *Konduktometrische Titrationen*, Theodor Steinkopff, Dresden, 1923; G. Jander and O. Pfundt, *Die visuelle Leitfähigkeitstitration*, 2d ed., Verlag Enke, Stuttgart, 1934; H. T. S. Britton, *Conductometric Analysis*, D. Van Nostrand Co., New York, 1934. See also I. M. Kolthoff and H. A. Laitinen, *The Determination of pH. Electrometric Titrations.*

1. The conductance may decrease
2. The conductance may remain unchanged
3. The conductance may increase.

If one of the products of the reaction is slightly dissociated or insoluble, the reaction may be expressed by the equation:

$$\underset{\text{(ion to be determined)}}{B^+ + A^-} + \underset{\text{(reagent)}}{C^+ + D^-} \rightarrow \underset{\text{(insoluble or slightly dissociated)}}{BD} + A^- + C^+$$

Therefore, by the reaction between B^+ and D^- ions, the B ions are replaced by C ions during the titration.

CASE 1: The mobility of the B ions (λB) is greater than that of the C ions (λC). The conductance of the BA solution decreases upon the addition of the reagent CD. This case generally occurs in the titration of strong acids with strong bases, or in the reverse titration. The hydrogen and hydroxyl ions are distinguished from the other ions by a much greater mobility (Fig. 89).

CASE 2: λB and λC are equal. The conductance remains unchanged by the addition of CD until the equivalence point has been reached. This case is met with in most precipitation reactions. In the titration of silver nitrate with barium chloride, the barium ion takes the place of the silver ion; and as both ions have about the same mobility, the conductivity does not change during the reaction. If, instead of barium chloride, sodium chloride is used as a reagent, the conductivity decreases slightly, since λ_{Ag} is greater than λ_{Na} (Fig. 90). On the other hand, with potassium chloride as a reagent, the conductivity increases slightly because λ_{Ag} is less than λ_K.

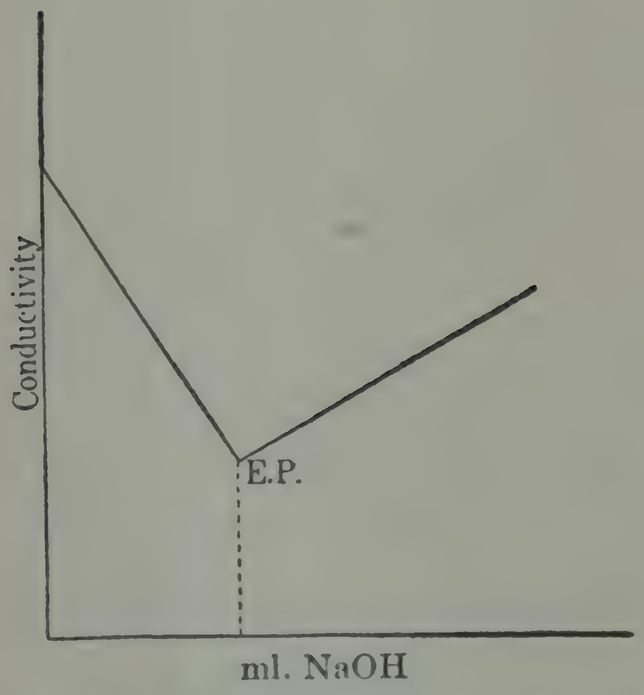


FIG. 89. Conductometric titration of a strong acid with a strong base.

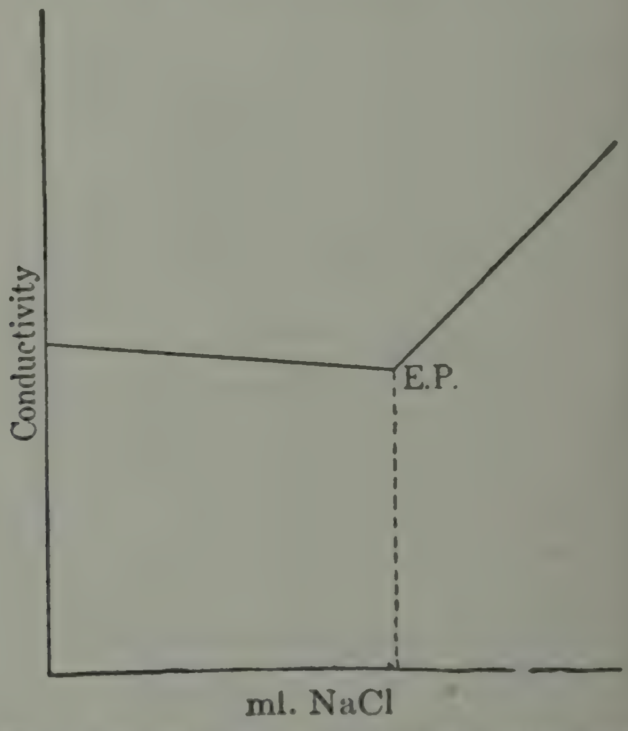


FIG. 90. Conductometric titration of silver nitrate with sodium chloride.

CASE 3: The conductivity increases from the beginning of the titration if a slightly dissociated substance is titrated and the reaction product is a strong electrolyte. This case generally occurs in the neutralization of a weak acid with a strong base, or a weak base with a strong acid. In any case the conductivity increases more strongly after the equivalence point has been reached, at least if the reagent is a strong acid or base.

In a conductometric titration the conductance is measured as already stated, after addition of successive amounts of reagent. The points thus obtained are plotted to give a graph which usually consists of two straight lines intersecting at the equivalence point. Therefore the latter is found graphically. In contrast to any other type of titration, measurements near the equivalence point have no special significance. As a matter of fact, the values found near the equivalence point are often worthless in the construction of the two straight lines, on account of the fact that the reaction product by its dissociation or solubility contributes to the conductivity of the solution, whereas we wish to locate the point at which the conductivity caused by the hydrolysis or solubility is negligible. In reactions which can be made the basis of a conductometric titration, the repression of the hydrolysis or solubility can be considered complete when there is an excess of the ion being titrated or of the reagent itself. Near the equivalence point, the points often do not lie on one of the two straight lines; the conductivity obtained is different from the corresponding values on the straight lines (titration of very weak acids and bases: hydrolysis; precipitation reactions).

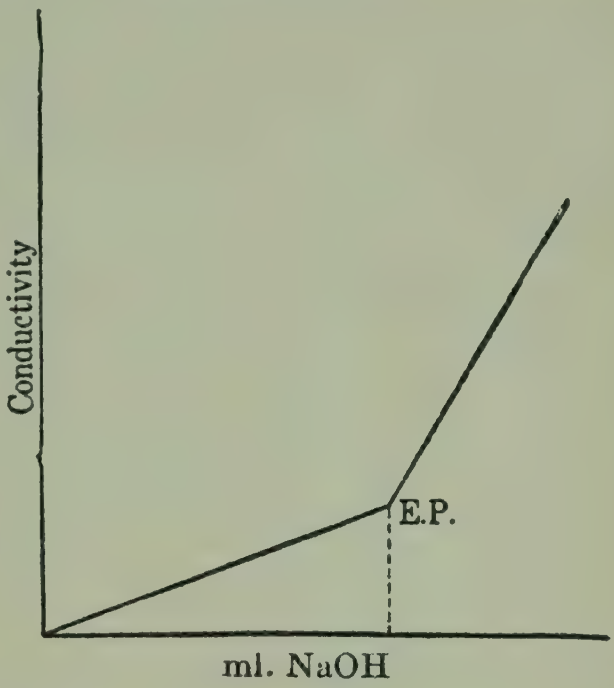


FIG. 91. Conductometric titration of boric acid with sodium hydroxide.

The fact mentioned, that a marked hydrolysis, solubility, or dissociation of the reaction product does not affect the accuracy of the method to any great extent, makes possible the application of *conductometric titrations to those cases in which other titration methods fail to give results.*

On the other hand, it must be emphasized that the conductometric method cannot be applied as generally as the ordinary, or potentiometric, on account of the fact that large amounts of foreign electrolytes which do not take part in the reaction affect the accuracy greatly. The relative change in the conductivity during the reaction, and upon addition of excess of reagent, mainly determines the accuracy; and this change is decreased by the presence of foreign electrolytes. Of course one must not infer from this that the conductometric method is rendered impossible by the presence of foreign electrolytes; if precise methods are used in the measurement of the conductivity and the titration is carried out in a thermostat, the method can be applied in the presence of relatively large amounts of indifferent electrolytes. This, however, is accomplished at the cost of the simplicity of the method.

An ordinary conductometric titration can be carried out in a relatively short time (ten minutes or longer).

Titration cells such as illustrated in Figures 92a and 92b can be used The two (platinized) platinum electrodes are set in a vertical position to prevent the deposition of precipitate in precipitation reactions. The electrodes are welded to a platinum wire, the latter being sealed in the glass and making electrical contact outside the vessel in a mercury pocket. The cell is placed in a block of wood or paraffin. Successive portions of the reagent are added from a micro buret. It is advisable to use a reagent solution which is at least ten to twenty times more concentrated than the solution to be titrated. The cell should contain a thermometer divided into 0.1° intervals. A change in temperature during the titration will affect the conductivity very much, because the latter increases greatly with increasing temperature (for most salts 2 to 2.5 per cent for 1°). In cases where the heat of reaction is fairly high, irregularities in the conductivity curve may occur on account of the temperature effect. As a rule, however, the heat effect during a titration is very small. After the addition of each portion of reagent the cell is shaken to secure a homogeneous solution; in this operation one must be careful not to warm the solution by taking the whole cell in the hand. Convenient for the shaking is a glass handle attached to the cell as in Fig. 92b. If work is done with solutions of quite different conductance, there should be available a number of titration cells with different cell constants adapted to the special work. The accuracy of the location of the end point in conductometric titrations as a rule is not better than 0.5 to 1 per cent. For precise work it is recommended that the titration be performed in a thermostat. In most practical work the use of a thermostat is unnecessary.

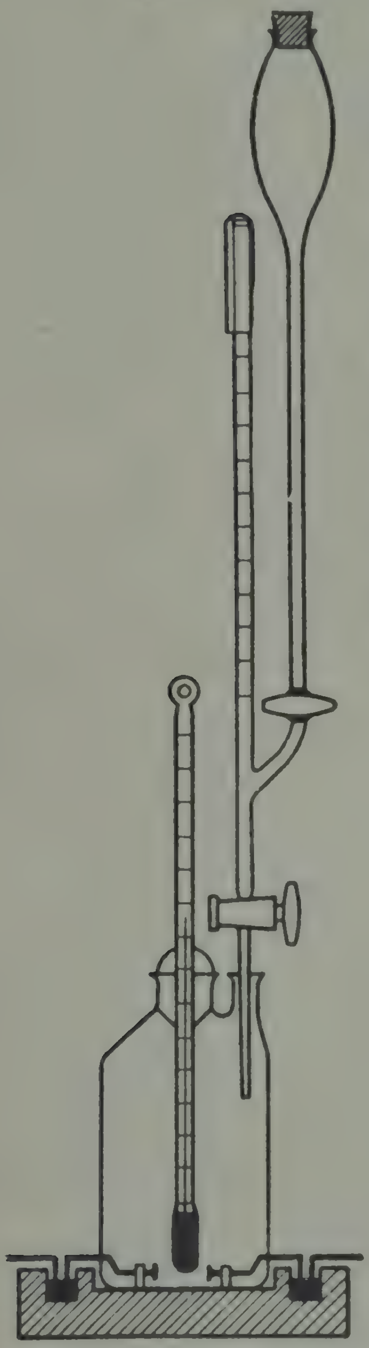


Fig. 92a. Cell for conductometric titrations.

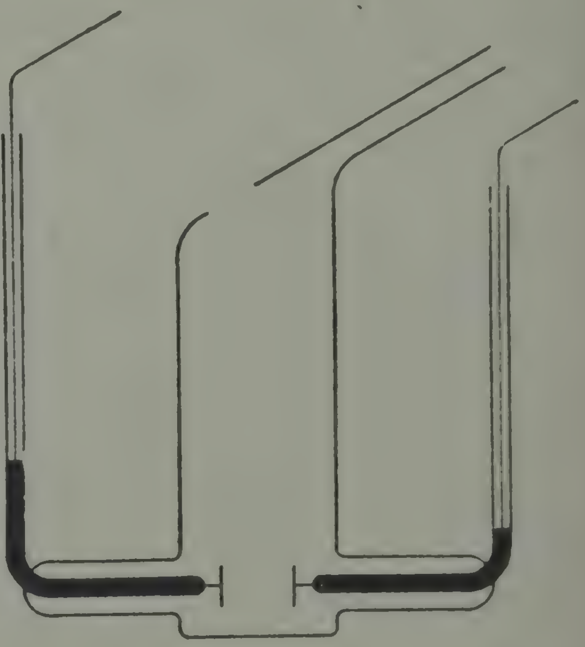


Fig. 92b. Cell for conductometric titrations (for use in thermostat).

Amperometric titrations.

In amperometric titrations application is made of electrolysis at a dropping-mercury electrode or a platinum-wire micro electrode. The former has been developed by Heyrovsky and his co-workers.[1] The principles underlying the use of the dropping-mercury electrode and the platinum micro electrode for analytical purposes are discussed below. Figure 93 is a schematic diagram of an electrolysis cell, containing a very dilute solution of thallous chloride in an excess of potassium chloride between two platinum electrodes, and a battery and rheostat by means of which the E.M.F. applied to the cell can be varied at will. The applied E.M.F. is gradually increased and the corresponding current through the cell is measured with the aid of an ammeter or a galvanometer (G). The values of the applied potential are then plotted against the corresponding values of the current. The resulting current-voltage curve has the general shape shown in Figure 94. The current remains very small, practically zero (residual current) until point A, called the decomposition voltage, is reached, after which it increases very rapidly as the applied E.M.F. is further increased ((BC) in Fig. 94). Under ideal conditions BC is a straight line whose slope is given by Ohm's law, $E_a - E_d = iR$, in which E_a is the total applied E.M.F., E_d is the decomposition voltage i the current, and R the resistance of the cell. During electrolysis, however, the concentration of the discharging ions decreases in the immediate neighborhood of the electrodes, and more or less "concentration polarization" results. Under these conditions the current-voltage curve deviates from a straight line, and its shape becomes that shown by the curve AC in Figure 95.

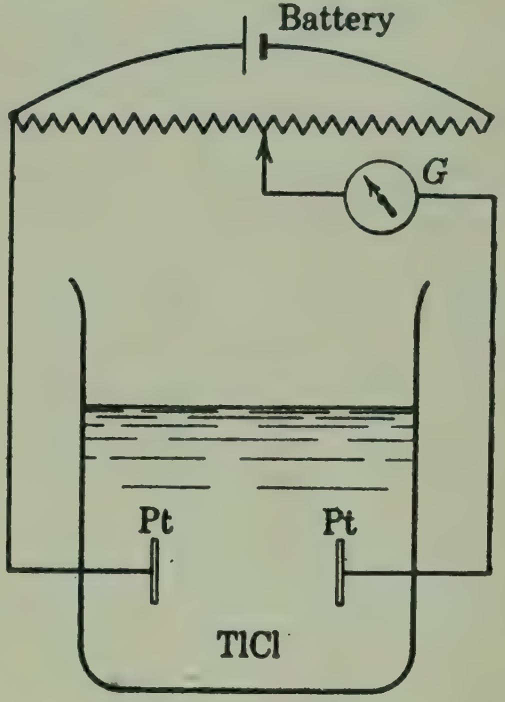


FIG. 93. Circuit for electrolysis experiment.

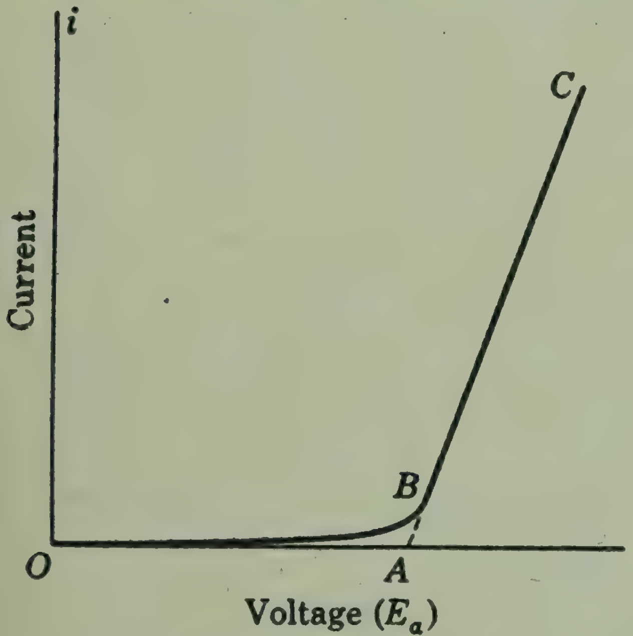


FIG. 94

Now consider the case in which the anode consists of a large platinum electrode or, better, a large silver-silver chloride electrode and the cathode is a small platinum wire. When a thallous chloride solution is electrolyzed, the potential of the large silver-silver chloride electrode is fixed as long as the current remains small; and it will remain constant, independent of the applied E.M.F. (depolarized electrode). With increasing applied E.M.F. the small platinum electrode remains polarized until the applied E.M.F. is equal to the decomposition voltage E_d, at which point the small electrode becomes depolarized and electrolysis starts. With increasing E.M.F. the current should increase according to *AB* (Fig. 95), if no polarization occurs. However, since the cathode is a small platinum wire, there will be a depletion of thallium ions around the electrode, concentration polarization results, and therewith an increase in the decomposition voltage (curves *AC* and *ADE*). After a few minutes, a steady state is set up, and the current remains constant when the applied E.M.F. is not changed. With further increase of the E.M.F. the depletion of thallium ions around the electrode becomes greater and finally practically complete. From then on (point *D* on the curve *ADE*) the current will remain constant as the applied E.M.F. is increased (*DE* is horizontal). This constant current, called the *diffusion current*, i_d, is proportional to the concentration of thallium ions in the solution.[1]

---

[1] For a review of the polarographic method and literature, see J. Heyrovsky *Polarographie*, in Vol. II of Böttger's *Physikalische Methoden der analytischen Chemie*, Akademische Verlagsgesellschaft, Leipzig (1936); for a complete discussion of the subject see I. M. Kolthoff and J. J. Lingane, *Polarography* (*Polarographic Analysis and Voltammetry, Amperometric Titrations*), Interscience Publishers, Inc., New York, 1941.

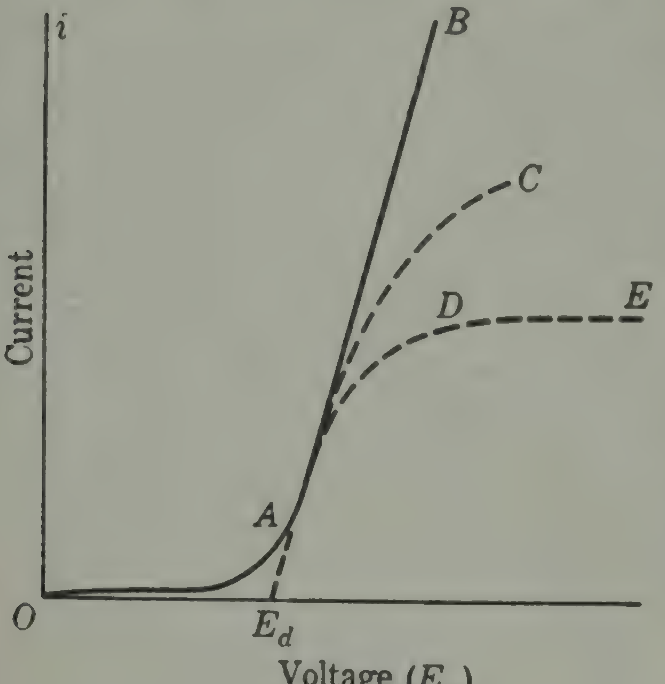


FIG. 95

When instead of the platinum micro electrode a dropping-mercury electrode is used as a cathode, similar current voltage curves are obtained. The current varies during the growth of a drop, but this causes only slight fluctuations in the deflection of the galvanometer, when this current-indicating instrument has a great inertia. The dropping electrode has the advantage over the platinum electrode that the measurements are made without waiting until the final stationary state is reached. With the dropping electrode no true steady state is reached, but the average current measured corresponds to a perfectly *reproducible* state.

The shape of a current-voltage curve obtained at the dropping-mercury electrode is shown in Figure 96. *OA* is again the residual current; the electroreduction starts at *A*, while at point *B* the current has become equal to the diffusion current i_d. The potential at point *D*, at which the current is equal to one half of the diffusion current (half wave potential), is characteristic of the particular electroreduction process and is in general independent of the concentration. At constant speed of dropping and constant drop size, the magnitude of the diffusion current is governed solely by the speed of diffusion of reducible matter up to the dropping cathode. *Therefore at constant temperature the diffusion current is proportional to the concentration of the electroreducible ions or uncharged reducible substances in*

---

[1] Compare H. A. Laitinen and I. M. Kolthoff, J. Am. Chem. Soc. *61*, 3344 (1939).

the bulk of the solution. This relation forms the basis of the analytical application of the polarographic method.

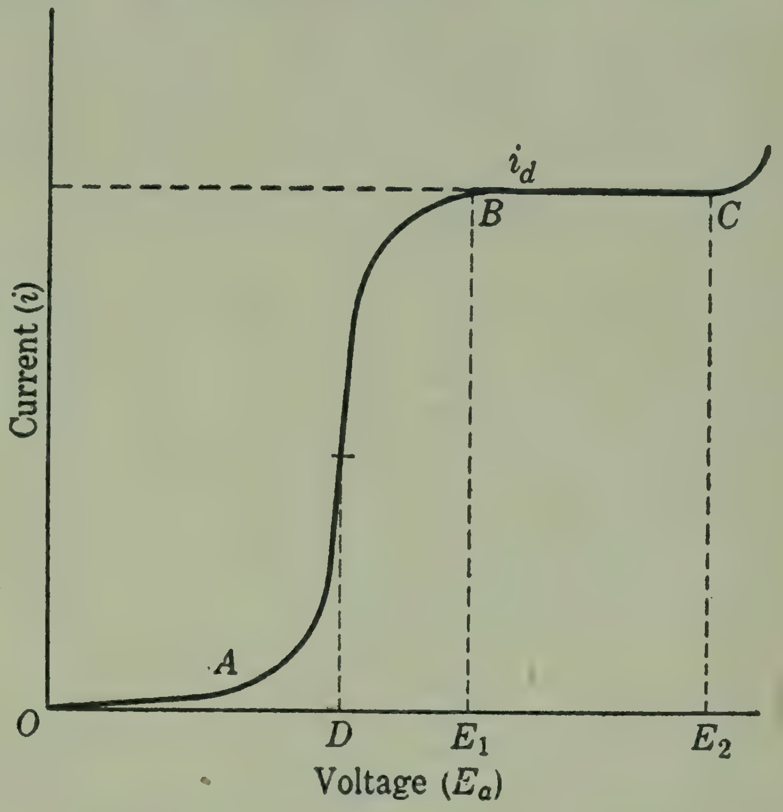


FIG. 96. Current-voltage curve obtained at the dropping-mercury electrode.

Now consider a solution of a reducible substance A, whose concentration is being gradually diminished by the addition of small portions of a reagent B which forms a slightly soluble compound AB. We will first assume that reagent B is not reduced at an applied E.M.F. between E_1 and E_2 (Fig. 96) at which A yields a diffusion current. The titration is begun at an applied E.M.F. between E_1 and E_2, and the current is measured after successive additions of reagent B. Since the current is proportional to the concentration of A in the bulk of the solution, it will be found to decrease continuously during the titration. When the current is plotted against the volume of reagent added and a correction is made for the dilution effect caused by the addition of reagent, a straight line is found (ABC in Fig. 97). The dilution correction is simply made by multiplying the values of the current measured by a factor $\frac{V + v}{V}$, in which V is the original volume and v is the volume of the reagent added. In order to keep this correction small, the concentration of the reagent should be 10 to 50 times greater than that of the solution titrated; the reagent is added from a micro buret. If the solubility of precipitate AB is less than 10^{-5} to 10^{-6} molar, its contribution to the diffusion current is negligibly small. In such a case the current will decrease according to ABC (Fig. 97), C corresponding to the end point. Upon further addition of reagent the current remains unchanged (CEF). If the solubility of AB is not negligibly small, its contribution to the diffusion current at the end point C is given by CD in Figure 97. From the practical point of view it is very advantageous that even under such conditions the amperometric titration yields excellent results. As a result of the suppression of the solubility by the common ion effect, the solubility becomes negligibly small in the presence of a reasonable excess of A or of B. In

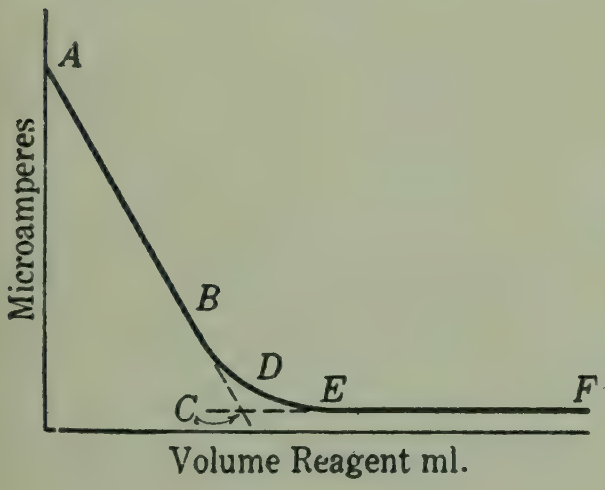


FIG. 97

such a case only those points are determined which lie on the straight lines, *AB* and *EF*. By determining three or four points on the precipitation line *AB* and a similar number of points on the reagent line *EF*, the end point *C* is found graphically with satisfactory accuracy. Such amperometric titrations yield accurate results even in highly dilute solutions.

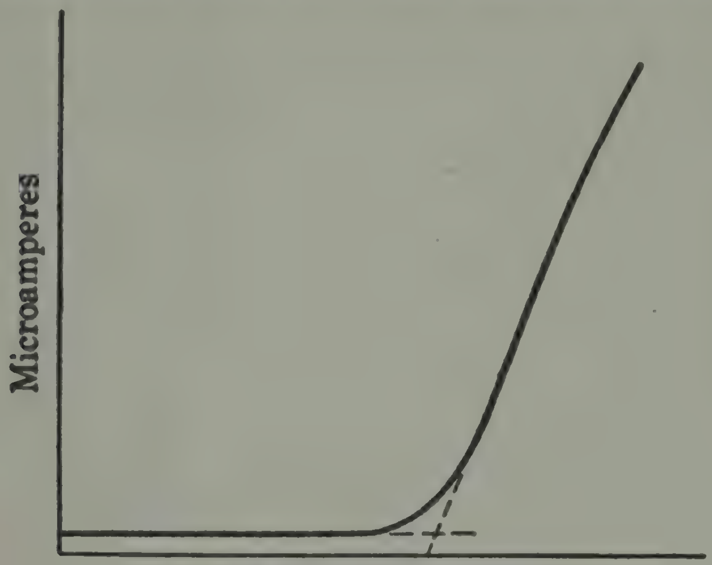


FIG. 98

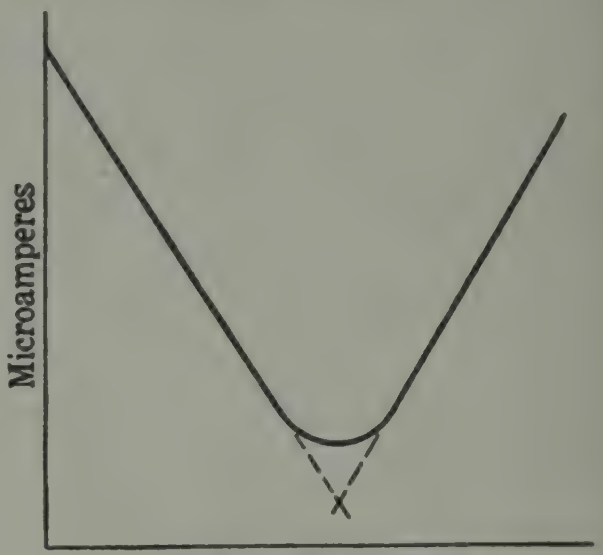


FIG. 99

When the substance titrated is not reduced at the applied E.M.F., but the reagent is, the titration lines are just the reverse of those given in the previous case (Fig. 98). Thus it has been found possible [1] to titrate sulfate solutions with lead nitrate with a high degree of accuracy at an applied E.M.F. at which lead yields a diffusion current.

When both the substance titrated and the reagent yield a diffusion current at the applied E.M.F., the titration lines have the shape given in Figure 99. Such titration lines are obtained, for example, in the titration of dilute lead solutions with chromate [2] or in the titration of nickel with dimethylglyoxime.[3]

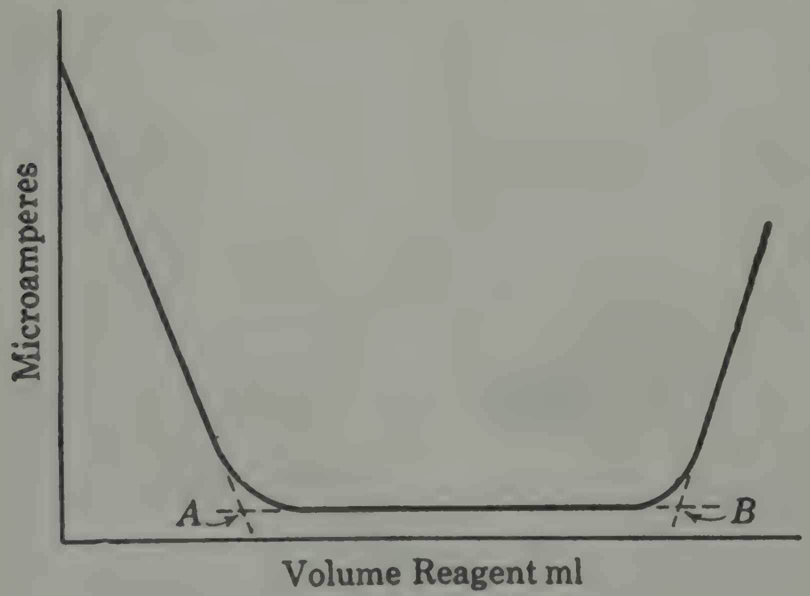


FIG. 100

Fractional-precipitation titrations can also be carried out amperometrically. Suppose that there are in the solution two ions *A* and *B* which yield insoluble salts with the reagent and that *B* does not start to precipitate until practically all of *A* is precipitated. We will further assume that *A* and the reagent yield a diffusion current at the applied E.M.F., while *B* is not reduced at this potential. It is easily seen, then, that the titration line will have the shape given in Figure 100. Point *A* corresponds to complete precipitation of A, and point B to that of B. Provided that A does not coprecipitate with B, the fractional-precipitation titration should yield useful analytical results.

---

[1] I. M. Kolthoff and Y. D. Pan, J. Am. Chem. Soc. *62*, 3332 (1940).

[2] *Ibid.*, *61*, 3402 (1939.)

[3] I. M. Kolthoff and A. Langer, J. Am. Chem. Soc. *62*, 211 (1940).

Amperometric titrations are not limited to precipitation reactions but can also be applied to neutralization, complex-formation, and oxidation-reduction reactions.[1]

From the historical viewpoint it may be mentioned that Heyrovsky[2] was the first to apply an amperometric titration to the determination of barium with sulfate. Heyrovsky suggested the name *polarographic titration.* Majer,[3] studying the titration of sulfate with lead, proposed the name *polarometric titration.* As it is the current which is measured during the titration, the term *amperometric titration* is preferable.

Amperometric titrations have certain limitations. Suppose that the three reducible substances A_1, A_2, A_3 are present in the solution (Fig. 101). A_1 is reduced at the potential E_1, giving the diffusion current i_1, proportional to the concentration of A_1; A_2 is reduced at the potential E_2, giving the diffusion current i_2; and A_3 is reduced at the potential E_3, giving the diffusion current i_3. Now suppose that a titration of (or with) A_1 is to be carried out in the presence of any amount of A_2 and A_3. If the applied E.M.F. is kept between E_1 and E_2, only A_1 is reduced, and the current is proportional to the concentration of A_1 alone, A_2 and A_3 being without influence. However, if A_2 is titrated in the presence of A_1, the current is the sum of the diffusion currents of A_1 (i_1) and the diffusion current and A_2 (i_2), the latter decreasing continuously during the titration. With increasing ratio of $\frac{i_1}{i_2}$ the accuracy in the measurement of i_2 becomes smaller. If A_3 is titrated, analogous considerations apply. For example, it is not readily possible to carry out the amperometric titration of sulfate with barium (or the reverse) in the presence of large amounts of metal ions more noble (more easily discharged) than barium, e.g., zinc, cadmium, nickel, cobalt, etc. In such a case, E_3 of Figure 101 would correspond to the discharge potential of barium and E_1 and E_2 to those of cadmium and zinc for instance. In this case it would be better to use a lead solution instead of barium, since the discharge potential of lead is found at a potential more positive than E_1.

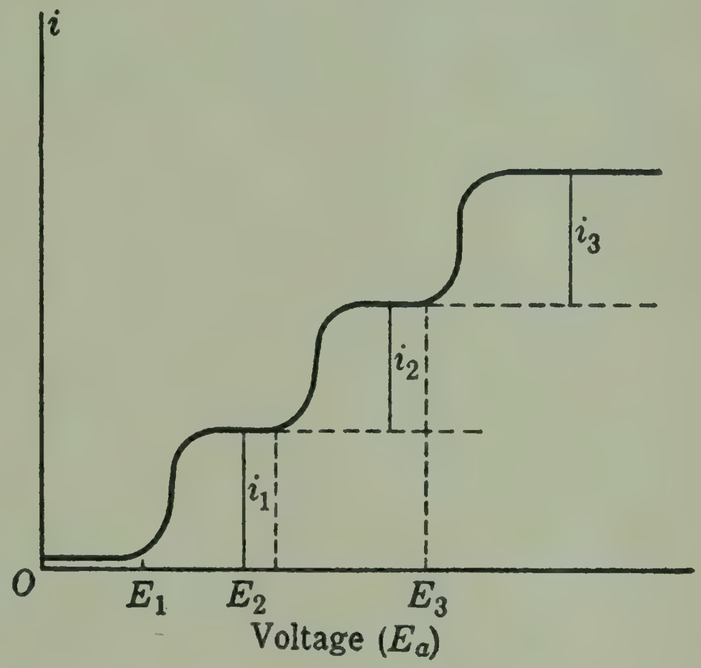


FIG. 101. Current-voltage curve of three reducible substances.

---

[1] For a complete review, see I. M. Kolthoff and J. J. Lingane, *Polarography* (1941).

[2] J. Heyrovsky, Bull. soc. chim. *41*, 1227 (1927); J. Heyrovsky and S. Berezicky, Collection Czechoslov. Chem. Commun. *1*, 19 (1929).

[3] V. Majer, Z. Elektrochem. *42*, 120, 123 (1936).

It is to be expected that many organic reagents which yield precipitates with metals will be useful in amperometric titrations. For example, nickel can be titrated with dimethylglyoxime; cobalt, copper, and palladium with α-nitroso-β-naphthol; and copper with benzoinoxime.

Under certain conditions amperometric titrations can be carried out by using a rotating micro electrode of platinum wire as the indicator electrode.[1]

For example, the titration of arsenic trioxide with bromate in acid medium can be made with high precision and accuracy even when the concentration of arsenic is as small as 10^{-4} *N*. The same is true of the titration of arsenic trioxide with iodine or the reverse titration.

It may be expected that in the future amperometric titrations will play an important rôle in volumetric analysis.

---

[1] H. A. Laitinen and I. M. Kolthoff, J. Phys. Chem. *45*, 1061, 1079 (1941).

PRACTICAL PART

CHAPTER XXXIII

VOLUMETRIC APPARATUS AND ITS USE

Common volumetric glassware.

The commonly used articles of volumetric glassware [1] are flasks, pipets, and burets.

Flasks. A volumetric flask is a flat-bottomed pear-shaped vessel with a long narrow neck (Fig. 102). A thin line etched around the neck indicates (usually) a certain volume of liquid that is held at some definite temperature, and the flask is then said to be graduated to *contain*. A flask may also be marked to indicate a certain volume of liquid that will be delivered if the liquid is poured out under specified conditions, and then it is graduated to *deliver*. Flasks graduated to contain are used much more frequently than those graduated to deliver; the latter are not suitable for exact work because it is virtually impossible to deliver the same volume every time.

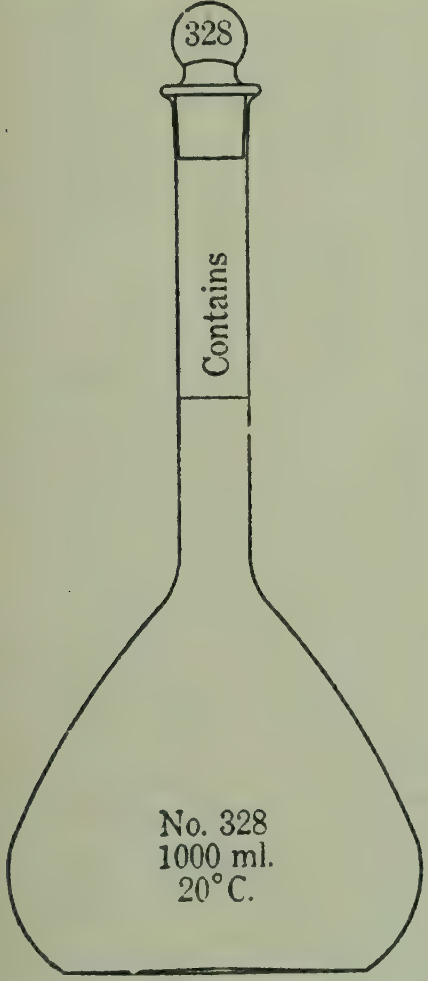


FIG. 102. Volumetric flask.

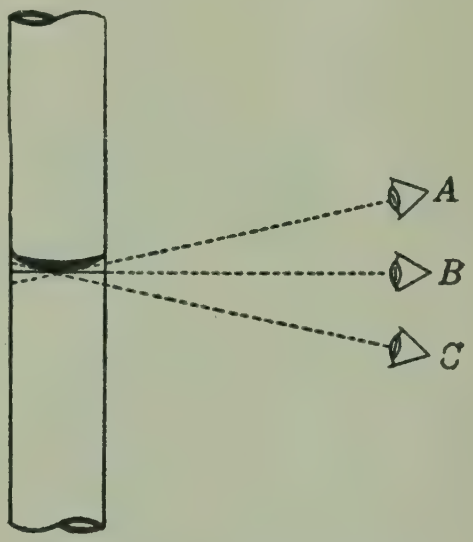


FIG. 103. Errors due to parallax in reading the level of a liquid in a graduated tube. *A*, meniscus reads too high; *B*, correct position of eye — no parallactic error; *C*, meniscus reads too low.

Since the graduation extends completely around the neck of the flask, it is a simple matter, when making the liquid up to the mark, to avoid errors due to parallax [2] by aligning the eye and the mark so that the nearer and farther side of the ring are tangent to the lower edge of the meniscus. The neck

---

[1] For an extensive treatment see V. Stott, *Volumetric Glassware*, H. F. and G. Witherby, London, 1928.

[2] Parallax: The apparent displacement of an object as seen from two different points. It is evident that parallax will give rise to errors in reading the position of the meniscus of a liquid in a marked or graduated tube if the line of sight of the observer is not at right angles to the tube (Fig. 103).

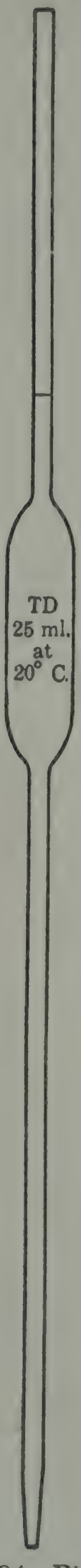


Fig. 104. Pipet.

of a volumetric flask is made comparatively narrow so that a small change in volume of liquid will cause a considerable difference in the height of the meniscus; the error made in adjusting the meniscus to the mark will consequently be very small. The distance from the mark to the stopper should be relatively great in order that there may be sufficient room for mixing after the volume has been made up to the mark. Volumetric flasks should be fitted with glass stoppers. The commonly used sizes are 50, 100, 250, 500, 1000, and 2000 ml.

Volumetric flasks are used for preparing solutions of known concentrations. The required amount of substance is weighed or measured out and transferred to a flask, water is added, and the volume is made up to the mark at a known temperature.

Pipets. Common pipets are cylinders drawn out at each end into narrow open tubes (Fig. 104). The upper limb of a pipet has a ring engraved upon it which fixes the volume of liquid that will be delivered if the pipet filled to this mark is allowed to deliver under certain specified conditions. The method of use is described later. A pipet used in this way to measure out one definite volume of liquid is known as a transfer pipet. Measuring pipets (Fig. 105) are narrow tubes subdivided into many divisions, which are employed for measuring out variable amounts of liquid. They do not find much application in exact work.

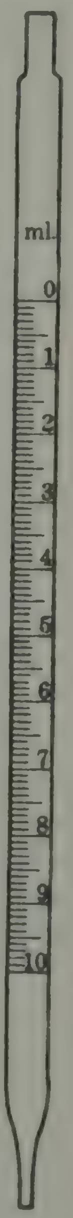


Fig. 105. Measuring pipet.

The orifice of a pipet must be made of such size that the outflow of liquid does not take place too rapidly, for otherwise errors due to slight differences in drainage time will become too pronounced. Pipets of 10, 25, and 50 ml. capacity are the most frequently used.[1]

Burets. Burets are long, graduated tubes of uniform bore provided at their lower ends with an arrangement for permitting easy control of outflow of liquid. They are used for delivering variable amounts of liquid and are therefore subdivided into many small divisions. Burets find their most extensive use in *titrations*. The 50 ml. buret graduated into tenth-milliliters is most often employed.[1] Burets with glass stopcocks (Geissler), Figure 106, are to be preferred, and are necessary for some liquids (for example, iodine solutions); strongly alkaline solutions are likely to cause the stopcock to stick and usually should not be used in these burets.[2] Burets in which the outflow of liquid is regulated by a pinchcock closing a section of rubber tubing attached to the end of the buret and provided with a glass nozzle (Fig. 107) are used for alkaline solutions and as cheap substitutes for glass-stopcock burets. The use of this form of buret for most solutions is not to be recommended on account of possible changes of level of liquid in the buret owing to changes in the elasticity of the rubber, as well as attack of the rubber by the liquid.

---

[1] Regarding Stas pipets, see Stas, *Œuvres complètes*, Vol. I, p. 830; I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis*, Vol. II, Interscience Publishers, Inc., New York, 1943.

Burets should be engraved with graduations extending halfway around the tube, so that parallactic errors can be easily avoided. To aid in reading the position of the meniscus, devices such as illustrated in Figure 108 are used. These cause the bottom of the meniscus to be darkened and sharply outlined against the white background, so that the level of the liquid can be read with great exactness.[3] Burets are always read to 0.01 ml. by estimation, when graduated to 0.1 ml.

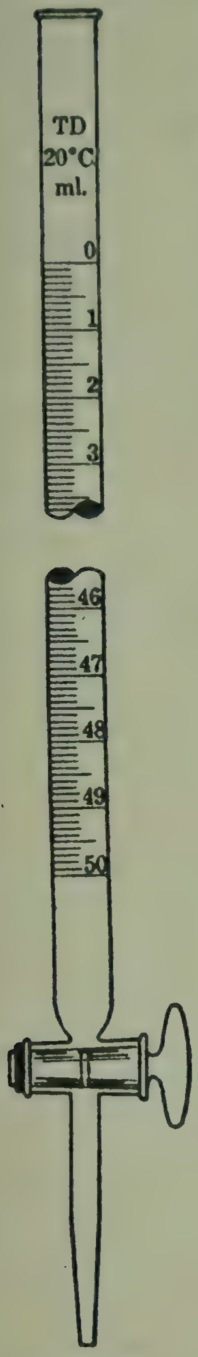


FIG. 106. Buret.

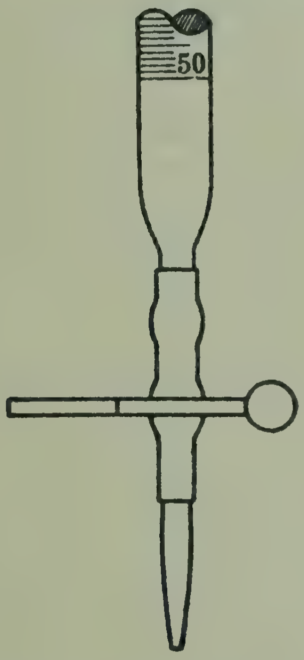


FIG. 107. Buret with pinchcock.

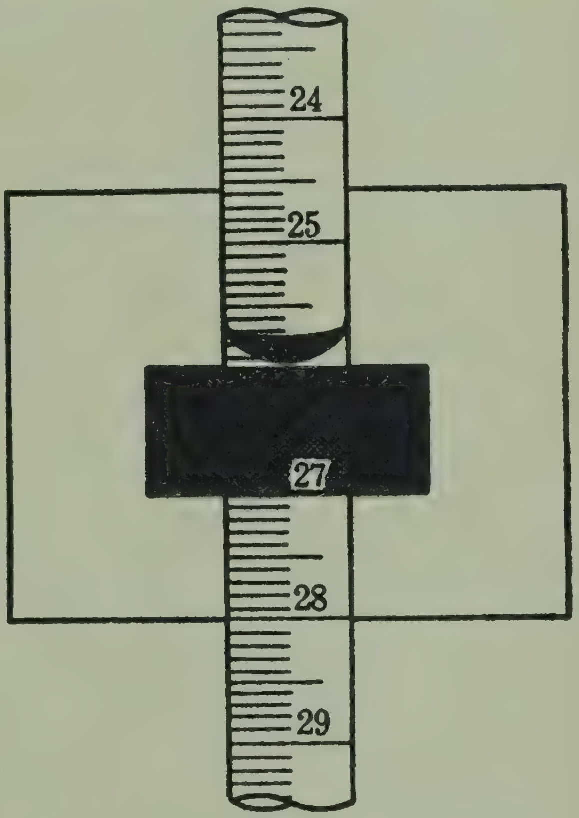


FIG. 108. Card for reading meniscus in a graduated tube (the upper edge of the dark portion should be placed ca. 1 mm. below the meniscus).

The glass stopcock of a buret must be lightly lubricated so that it turns easily (regarding the lubricant see p. 190). Too much grease must be avoided

---

[1] It would be advantageous to have burets graduated slightly beyond 50 ml., say to 55 ml. Then it would be possible to take 50 ml. of a standard solution with a pipet for titration without fear of having to refill the buret if the titrating solution were slightly weaker.

[2] Burets with metal (nickel) stopcocks are excellent for strongly alkaline solutions.

[3] When the liquid is strongly colored, as is the case, for example, with potassium permanganate solution, the upper edge of the meniscus must be read.

— it is likely to plug the stopcock or the tip. Burets are filled with the aid of a buret funnel, which should be removed after the filling.

For micro and semi-micro work, burets of 1 to 10 ml. capacity graduated to 0.01 or 0.02 ml. are employed.

Specifications for volumetric glassware.

The following excerpts are taken from U. S. Bureau of Standards Circular No. 9, 1916:

The outlet of any transfer pipet must be of such size that the free outflow shall last not more than one minute and not less than the following for the respective sizes:

MINIMUM OUTFLOW TIME FOR PIPETS

Capacity (in ml.) up to and including . .	5	10	50	100	200
Outflow time (in seconds)	15	20	30	40	50

The rate of outflow of burets and measuring pipets must be restricted by the size of the tip, and for any graduated interval the time of free outflow must not be more than three minutes nor less than the following for the respective lengths:

MINIMUM OUTFLOW TIME FOR BURETS

LENGTH GRADUATED, CM.	TIME OF OUTFLOW, SEC.	LENGTH GRADUATED, CM.	TIME OF OUTFLOW, SEC.
70	160	35	60
65	140	30	50
60	120	25	40
55	105	20	35
50	90	15	30
45	80		
40	70		

TOLERANCES

(a) Flasks

CAPACITY (IN ML.) LESS THAN AND INCLUDING	LIMIT OF ERROR, ML.	
	If to Contain	If to Deliver
25	0.03	0.05
50	0.05	0.10
100	0.08	0.15
200	0.10	0.20
300	0.12	0.25
500	0.15	0.30
1000	0.30	0.50
2000	0.50	1.00

(b) Transfer Pipets

Capacity (in ml.) Less than and Including	Limit of Error, ml.
2	0.006
5	0.01
10	0.02
30	0.03
50	0.05
100	0.08
200	0.10

(c) Burets and Measuring Pipets

Capacity (in ml.) of Total Graduated Portion Less than and Including	Limit of Error (in ml.) of Total or Partial Capacity	
	Burets	Measuring Pipets
2	....	0.01
5	0.01	0.02
10	0.02	0.03
30	0.03	0.05
50	0.05	0.08
100	0.10	0.15

Cleaning volumetric glassware.

It is highly important that all volumetric apparatus be scrupulously clean and that the inside walls be entirely free from grease. Water will not uniformly wet a glass surface that is contaminated with any fatty substance; and when water or an aqueous solution comes into contact with such a surface, droplets will adhere when the water drains away, or if a film is formed at first, it will soon break and leave patches of liquid. Moreover the meniscus of a solution will be distorted if the neighboring walls are greasy. Upon a clean, grease-free glass surface water spreads, and leaves an invisible film when it is allowed to run off. It is obvious that no exact measurements of volume can be made if the walls of the apparatus are greasy even to the slightest extent. Therefore, before any volumetric work is attempted, the walls of the measuring vessel should be examined for greasiness, and the vessel cleaned if water does not uniformly wet the surface.

There are a number of cleaning agents that can be used for removing grease films from glass surfaces. A solution of sodium or potassium dichromate in concentrated sulfuric acid (p. 235) is commonly used for the purpose and is effective in most cases. The article to be cleaned is filled with the cold cleaning solution and allowed to stand for a few hours, or overnight if the glass is very greasy. Sometimes a shorter period of contact is sufficient. Large flasks are cleaned by pouring in a small volume of the solution, inverting, and shaking at intervals so that the walls are kept continuously wetted. Pipets are kept filled with the cleaning mixture by attaching a piece of rubber tubing to the top of the suction tube and closing it with a pinch clamp. Great care must be taken when filling pipets not to get the corrosive liquid into the mouth. It is best to interpose a safety bottle between the pipet and the mouth, or to use the suction line. Burets are likewise allowed to stand filled with the cleaning mixture.

A solution of potassium hydroxide in alcohol is a very good cleaning agent; it is more rapid in its action than chromic-sulfuric acid and is used in those cases in which the latter is ineffective. This alkaline liquid — and other strongly alkaline solutions as well — should not be allowed to remain in contact with glass for any great length of time because of the slow attack on the glass. An aqueous solution of sodium hydroxide containing potassium permanganate is also very effective. It may be left in the glass vessel for five or ten minutes. Manganese dioxide will separate on the glass at the places where it is contaminated with grease or other organic substances; the coating of the dioxide is removed by rinsing with strong hydrochloric acid; the chlorine thus formed aids in removing the organic material. A dilute acid solution containing sulfite may also be used for removing the manganese dioxide.

Whatever cleaning solution is used, the vessel is finally rinsed out carefully, first with tap water and finally with distilled water, and allowed to drain. If the glass has been entirely freed from fatty substances, the walls will be uniformly wetted and a thin film will remain. It is usually not necessary, nor even advisable, to dry volumetric vessels before use.

Calibration of volumetric apparatus.

Necessity for calibration. Ordinary volumetric glassware should always be tested for accuracy before use, for the errors of graduation may exceed the permissible errors of a determination. Indeed, no matter how accurate a piece of glassware is stated to be, the user should always test it for himself and be assured beyond all doubt that it is sufficiently accurate for the work in hand.

Unit of volume. The unit of volume in the metric system is the liter. The *liter* (l.) is defined as the volume occupied by a *mass* of one kilogram of water at the temperature of maximum density (3.98° C.) and under normal atmospheric pressure.[1] The one-thousandth part of the liter is called the *milliliter* (ml.).

It should be noted that the fundamental unit of volume is not based upon the cubic decimeter, which would appear to be the logical unit, since it is derived from the unit of length, the meter. It was originally intended that the mass of the kilogram should be equal to that of one cubic decimeter of water at its temperature of maximum density. On account of experimental difficulties this simple relation was not quite realized, and it has been shown that one liter is equivalent to 1.000028 cubic decimeters or 1000.028 cubic centimeters[2]

---

[1] *Travaux et mémoires du Bureau International des Poids et Mesures*, Vol. XII (1902). The pressure is specified because of the compressibility of water.

[2] C. E. Guillaume, *La creation du Bureau International des Poids et Mesures et son œuvre*, p. 258, Paris, 1927.

(cc.). It has been the custom to use the terms *cubic centimeter* and *milliliter* interchangeably, and this usage still generally persists. Since the unit of volume is the liter and volumetric glassware is calibrated on the basis of this unit, volumes should always be expressed in terms of milliliters and not of cubic centimeters. For most purposes the difference between a cubic centimeter and a milliliter is so small, amounting to only one part in 35,000 approximately, that no harm is done in calling a milliliter a cubic centimeter; but it should be remembered that the term *cubic centimeter* is not the proper designation, and its use for this purpose should be discontinued.

General method of calibration. Volumetric glassware is generally calibrated, or tested for accuracy, by weighing the amount of pure water held or delivered at a given temperature and calculating the volume therefrom. Indirectly, the volume of a vessel can be determined by comparing its volume with that of a vessel which has been calibrated by the direct method. The first method is the better.

Before entering upon the method of deriving the volume of a vessel from the weight of water held, it is important to realize that (1) the density of water varies with the temperature, (2) the volume of a glass vessel varies with the temperature, (3) the water filling the vessel is weighed in air.

It is first of all necessary to choose a temperature at which the vessel will hold the designated volume. A flask holding exactly one liter at one temperature will no longer do so at any other temperature. Therefore a definite temperature must be decided upon as the *standard temperature* for volumetric glassware. The standard temperature chosen should be close to the average laboratory temperature at which the apparatus is used. In the United States the temperature of 20° C. has been designated by the Bureau of Standards as the standard temperature for glassware. Therefore, in the United States, the calibrated vessel will hold the nominal volume at 20°; above 20° it will hold more than the designated capacity, and below 20° it will contain less.

Having decided upon the temperature at which the vessel shall hold the designated volume, it remains to derive the capacity at this temperature from the weight of water, determined in air with brass weights, held at any laboratory temperature. In the great majority of cases the temperature of the laboratory will not be exactly 20° and the calibration must be carried out by weighing the water in the apparatus at some temperature other than 20°. In order to calculate the volume of the vessel at the *temperature of the measurement*, it is necessary to know the density of the water at the temperature in question. By dividing the *mass* of the water by the density, the volume is directly obtained at the temperature of measurement. It must be noted that the *mass* of the water is required. The mass of the water is obtained from its weight in air by reducing the weight to *vacuo*. For the latter calculation it is necessary to know, besides the density of the water, the density of the weights and the density of the air. The weights used in weighing large volumes of water are usually made of brass, and the density of brass may be taken equal to 8.4 (in very exact work the density must be determined). The density of the air can be calculated if the temperature, barometric pressure, and humidity are known. The following formula applies:

$$d_a = \frac{0.0012931\,p - 0.00049\,h}{760(1 + 0.00367\,t)},$$

where d_a = density of air (g./ml.)
p = atmospheric pressure in mm. of mercury (reduced to 0° C.)
h = aqueous tension of the atmosphere in mm. of mercury [1]
t = temperature in degrees Centigrade.

In the great majority of cases it suffices to assume that the density of the air is 0.0012 g. per ml. and to calculate the air buoyancy on this assumption. Results of sufficient accuracy are then obtained for all ordinary careful analytical work.

To make the calculation entirely clear, let us take a specific example. Suppose a liter flask to be filled to the mark with water at 22° (the laboratory temperature) and the weight of the water found to be 997.00 g. (weighing made by substitution). The mass, or vacuum weight, of the water weighing 997.00 g. in air is approximately $997.00 + 0.0012\left(\frac{997.0}{0.998} - \frac{997.0}{8.4}\right) = 997.00 + 1.06 = 998.06$, or 998.1 g. The density of water at 22° is 0.99780 g./ml. (Table LXXII, p. 764). Therefore the volume of the water, and the volume of the flask at 22°, is $\frac{998.1}{0.9978} = 1000.3$ ml.

After the volume has been found for any particular temperature, it still remains to calculate the volume of the vessel at the standard temperature of 20°. It is necessary for this purpose to know the coefficient of expansion of the material of which the vessel is made. The average coefficient of cubical expansion of glass is 0.000025 per degree Centigrade. The volume of a glass vessel at 20° is then readily obtained from its volume at any other temperature by using the following expression:

---

[1] h = (relative humidity) × (aqueous tension of air saturated with water vapor at temperature t).

$$V_{20} = V_t + 0.000025\,V_t(20 - t)$$

where V_{20} = volume of vessel at 20° C.
V_t = " " " " t° C.

The flask of the example above would have a volume of $1000.3 - (0.000025 \times 2 \times 1000.3) = 1000.3 - 0.05 = 1000.25$ ml. at 20°

To avoid the labor involved in making the calculations illustrated above, it is convenient to employ tables from which can be obtained directly the weight of water that must be weighed out at any temperature in air to give the desired volume of the glass vessel at 20°. Table LXVIII is an example of such tables.

TABLE LXVIII. CALIBRATION TABLE

TEMP. ° C.	VACUO WEIGHT OF 1000 ML. OF WATER	CORRECTION A	CORRECTION B	CORRECTION C	CORRECTIONS $A+B+C$	$1000 - (A+B+C)$	TEMP. ° C.
	g.	g.	g.	g.	g.	g.	
15	999.13	0.87	1.07	0.13	2.07	997.93	15
16	998.97	1.03	1.07	0.10	2.20	997.80	16
17	998.80	1.20	1.07	0.08	2.35	997.65	17
18	998.62	1.38	1.06	0.05	2.49	997.51	18
19	998.43	1.57	1.06	0.03	2.66	997.34	19
20	998.23	1.77	1.05	0.00	2.82	997.18	20
21	998.02	1.98	1.05	− 0.03	3.00	997.00	21
22	997.80	2.20	1.05	− 0.05	3.20	996.80	22
23	997.57	2.43	1.04	− 0.08	3.39	996.61	23
24	997.33	2.67	1.04	− 0.10	3.61	996.39	24
25	997.08	2.92	1.03	− 0.13	3.82	996.18	25
26	996.82	3.18	1.03	− 0.15	4.06	995.94	26
27	996.55	3.45	1.03	− 0.18	4.30	995.70	27
28	996.27	3.73	1.02	− 0.20	4.55	995.45	28
29	995.98	4.02	1.02	− 0.23	4.81	995.19	29
30	995.68	4.32	1.01	− 0.25	5.08	994.92	30
31	995.37	4.63	1.01	− 0.28	5.36	994.64	31
32	995.06	4.94	1.01	− 0.30	5.65	994.35	32
33	994.73	5.27	1.00	− 0.33	5.94	994.06	33
34	994.40	5.60	1.00	− 0.35	6.25	993.75	34
35	994.06	5.94	0.99	− 0.38	6.55	993.45	35

Explanation of Table LXVIII. The first column gives the laboratory temperature, i.e., the temperature of the water weighed and the glass vessels being calibrated. The column headed $1000 - (A + B + C)$ indicates the weight of water that must be weighed out with brass weights at the temperature of calibration and at normal atmospheric pressure (760 mm. of mercury) to furnish a volume of water that will indicate a capacity of one liter if the vessel is brought to the standard temperature of 20°; i.e., if this weight of water is contained in a flask and a mark is made at the meniscus, the flask so marked will hold exactly one liter at the temperature of 20°. The other columns of the table contain the corrections that must be applied to obtain the values in the last column. This table can be used for testing or calibrating vessels of any volume by taking proportional parts or multiples of the values for 1 liter.

How the table was constructed. In order to obtain the values in the next to the last column of Table LXVIII, it is necessary to take into account the density of the water at the temperature of calibration, the effect of the buoyancy of the air on the water and the weights, and the difference in volume of the glass vessel at the calibration temperature and at 20°. The corrections for these effects for various laboratory temperatures are given in the columns headed "Correction *A*," "Correction *B*," and "Correction *C*," respectively.

At any temperature above 4° it is necessary to weigh out less than 1000 g. of water to obtain a volume that will represent 1000 ml. The amount to be weighed out *in vacuo* at any temperature is evidently given by the expression 1000 *d*, where *d* is the density of the water at the working temperature. Values for 1000 *d* are recorded in the second column of the table. Values in the column "Correction *A*" indicate the weight in grams that must be subtracted from 1000 g. to give the weight of water *in vacuo* that would occupy a volume of 1000 ml. at the temperature indicated.

Since it is desired to make the weighings in air, we must determine from the vacuum weight the weight of water that must be weighed out *in air with brass weights* to give an amount of water that will have a volume of 1000 ml. at the calibration temperature. (1000 − *A*) g. of water weighed in air will occupy a volume greater than 1000 ml., because the density of water is less than that of the weights, and therefore the water displaces more air than the equal weight of brass, and accordingly the apparent loss in weight of the water is greater than that of the weights. It is necessary to weigh out in air (1000 − *A* − *B*) g. of water to furnish one liter, where *B* is the correction for the differential buoyancy of the air. The value of B is easily calculated. It is equal to the weight of air displaced by one liter of water less the weight of the air displaced by the weight of brass required to counterbalance the mass of water which represents a capacity of the glass vessel equal to one liter if the vessel is at the temperature of 20°:

$$B = \left[1000 - \frac{1000 - (A + B + C)}{8.4}\right] d_a.$$

In this expression, d_a is the density (g./ml.) of the air at the temperature and the pressure of the weighing. C is the correction factor for the expansion of the glass; it is explained below. Solving this expression for B, it is found that:

$$B = (7400 + A + C)\frac{d_a}{8.4 - d_a}.$$

In exact work the value of d_a is calculated from the temperature, the pressure, and the humidity of the air in the balance case at the time of the weighing by applying the formula given on p. 526. The value 8.4 for the density of the brass weights is an average value.

The values of B in Table LXVIII have been calculated on the assumption that the atmospheric pressure is 760 mm. of mercury, that the temperature of the air is the temperature of the water used in the calibration, and that the relative humidity of the air is 50 per cent. In the great majority of cases it is not necessary to take into account variations in the value of B caused by departures of pressure and humidity from these assumed values. If very accurate results are required, the exact value of B can be found by substituting in the equation the value for the density of the air at the time of the weighing. More approximately the corrected value of B can be found as follows:

Let B_t = the buoyancy correction when $p = 760$ and the water and the air have the same temperature t. This is the value given in the table
p = atmospheric pressure in millimeters of mercury
t_a = temperature of *air* when weighing is made
B'_t = buoyancy correction for atmospheric pressure p and temperature t_a.

Then

$$B'_t = B_t \times \frac{p}{760} \times \frac{1 + 0.00367\,t}{1 + 0.00367\,t_a}.$$

If the corrected value of B differs by less than 0.005 g. from the value of B in the table, it is useless to apply the correction, because the values for A, B, and C in Table LXVIII have been computed only to the nearest 0.01 g., i.e., to 1 part in 100,000, which is 0.001 per cent.

If $1000 - (A + B)$ g. of water are weighed out in air with brass weights, the volume of the water will be exactly 1000 ml.; and it follows that this will be the volume of the glass vessel at the temperature of the calibration. But the volume of the vessel at 20°

is desired. If the calibration temperature is above 20°, the indicated volume will be too small; and if below 20°, it will be too large. To take account of the expansion (or contraction) of the glass vessel when it is brought to 20° from the calibration temperature, it is necessary to introduce the correction C. The value of C evidently depends upon the coefficient of cubical expansion of the material of the vessel. The average coefficient of cubical expansion of glass is 0.000025 per degree Centigrade. Therefore a glass vessel which holds exactly 1000 ml. at $t°$ will hold $1000 + (20 - t)\ 1000 \times 0.000025$ ml. at 20°, and it follows that $1000 - [A + B + (20 - t)\ 1000 \times 0.000025]$ g. of water must be taken at the temperature t to indicate a capacity of 1000 ml. at 20°. The value of $(20 - t)\ 1000 \times 0.000025$ is the correction C, the values of which are given in the table for various temperatures. It is to be noted that for calibration temperatures above 20° the value of C is negative.

The sixth column in the table contains the sum of the corrections A, B, and C, and *the seventh column gives the values of* $1000 - (A + B + C)$, *furnishing directly the weight of water which must be taken at the given temperature to indicate, in a glass vessel, a volume of 1000 ml. at 20°.*

Illustrations of the use of the table.

1 a. What weight of water must be taken at 30° to calibrate a liter flask?

Ans. Reading opposite 30°, the value 994.92 g. is found in the next to the last column; this is the weight of water required.

1 b. What amount of water must be weighed out at 20° to calibrate a 250 ml. flask?

Ans. Value for 1000 ml. at 20° = 997.18 g. Therefore for the volume 250 ml., $\frac{250}{1000} \times 997.18 = 249.29(5)$ g. of water are required.

2. A liter flask was filled exactly to the mark at 23° and the weight of the water in the flask determined. It was found to be 996.70 g. What is the capacity of the flask at the standard temperature?

Ans. Reading opposite 23°, the total correction value, $A + B + C$, is found to be 3.39. The volume of the flask at 20° is therefore $996.70 + 3.39 = 1000.09$ ml.

3. A glass vessel holds 35.681 g. of water at 25°. What is the capacity of the vessel at 20°?

Ans. $\frac{35.681}{0.99618} = 35.817$ ml. The value 0.99618, the apparent density of water including the glass correction at 25°, is found by dividing 996.18 in the next to the last column by 1000

4. A liter flask is found to hold 996.39 g. of water at 24°. What is the capacity of the flask at 24°?

Ans. In this case the correction C must not be included. Therefore the volume of the flask at 24° is $996.39 + (A + B) = 996.39 + 2.67 + 1.04 = 1000.10$ ml.

5. A 500 ml. Pyrex flask filled to the mark contains 497.46 g. of water at 30°. What is the capacity of the flask at the standard temperature? The coefficient of cubical expansion of Pyrex is 0.000010.

Ans. C must be calculated: $C = 500 \times (-10) \times 0.00001 = -0.050$. Therefore the capacity of the flask at $20° = 497.46 + \frac{4.32}{2} + \frac{1.01}{2} - 0.05 = 500.08$ ml.

Directions for calibration.

The apparatus to be calibrated must be scrupulously clean and free from grease. The water and the glassware should be allowed to stand for some time in the room in which the calibration is to be made before the operations are begun in order that they may assume the temperature of the air. The room temperature should be as constant as possible to preclude the possibility of volume changes during the calibration. Ordinary distilled water is used; it need not be air-free. A thermometer graduated in single degrees is suitable for obtaining the temperature of the water. Temperatures should be read to the nearest 0.5°. In very accurate work the correctness of the thermometer should be checked; an error of 1° will lead to an error of approximately 0.02 per cent in the volume of the vessel. Care should be taken not to warm the apparatus by excessive handling.

Flasks. For the calibration of flasks having a capacity greater than 100 or 200 ml., a sturdy balance that will take a load of 2 kg. and which has a sensitivity of at least 0.01 g. at the maximum load should be available. The flask to be calibrated must first be dried. It is not permissible to hasten the drying by heating, for then slow changes in volume may occur after cooling. A stream of air may be passed into the inverted flask to hasten the evaporation of adhering water. The air for this purpose is best filtered through cotton wool to remove dust and oil droplets which may possibly be present in the compressed air (originating in the compressors). Flasks are quickly dried in this way if they are first rinsed once or twice with alcohol or, better, with acetone, to remove the water.

The water for the calibration of a flask must be weighed by substitution, because the rougher balances may have arms that are quite unequal in length. The procedure to be followed depends upon whether the flask is to be calibrated or simply tested for accuracy.

In the first case the flask is placed on the right-hand pan of the balance together with weights numerically equal to the nominal volume of the flask; e.g., for a liter flask 1000.0 g. would be taken. The flask and the weights are now tared by adding to the left-hand pan other weights, lead shot, or any other finely divided dense material. The nominal weight on the right pan is next removed, and a weight equal to $(A + B + C)$ (or its proportional part or multiple, as the case requires) is put in its place. Water is then poured into the flask until the original equilibrium is restored. In this operation care should be taken not to wet the neck of the flask. It is best to use a long-stemmed funnel. If drops adhere to the neck above the meniscus, they are removed with a roll of filter paper; such adhering drops will not form if the flask and the water are grease-free. The final adjustment of weight is conveniently made by adding or removing water with a long narrow glass tube or a pipet. When the adjustment has been made, the flask will contain a volume of water that indicates the capacity of the flask when the latter has a temperature of 20°. The flask is now removed from the balance, and a narrow strip of gummed label is pasted all around the neck to indicate the position of the meniscus. The upper edge of the label should be tangent to the lowest part of the meniscus. The strip of paper should be coated with a thin layer of paraffin, or with varnish, to protect it from water. If it is desired to mark the flask permanently, the neck is covered for some distance on either side of the strip with a thin coating of paraffin; and a ring is made all around the neck by scratching the paraffin with a sharp-pointed instrument in such a way that the glass is laid bare. By exposing the unprotected part of the glass to hydrofluoric acid vapors, a mark will be etched into the glass. The student should use the first method of marking, because the apparatus is loaned to him.

If it is desired to *test* a flask, i.e., to determine the capacity indicated by the mark already on the vessel, the same procedure as described above is followed in principle. The dry flask is tared with the nominal weight, the latter is replaced by $A + B + C$ or its proportional part, and the flask is then filled exactly to the mark with water. If the original equilibrium position of the balance is now restored, it is clear that the flask is exactly correct.

If equilibrium is not established, weights are added or removed until the flask is exactly balanced. The weights added or removed correspond to the difference in volume from the nominal volume, and the error of the flask is calculated therefrom.

It is immaterial whether a flask is calibrated or tested. The latter method possesses the advantage that a new mark need not be made; but then, on the other hand, a correction must be applied to every determination in which it is used, if the flask is found to be in error. If the student merely checks the accuracy of a flask, he must record the capacity in his notebook immediately, indicating also the number of the flask tested, so that there may be no possibility of confusing it with another. It is advisable to affix to the flask a small paraffined label bearing the true capacity.

Pipets. The pipet to be *tested* is filled above the mark with distilled water by applying gentle suction with the mouth and closing the upper end of the tube with the dry index finger, the tip is wiped off to remove any adhering droplets, and the water is then allowed to flow out slowly, while the end of the pipet is held against the wall of a beaker until the meniscus is brought into exact coincidence with the mark. The tip of the pipet is then brought into contact with the wall of the vessel in which the water is to be weighed (this vessel must be weighed beforehand to 0.005 g.). Small (50 or 100 ml.) Erlenmeyer flasks or large glass-stoppered weighing bottles are best used as containers for weighing the water. The pipet is allowed to deliver freely while held vertically with the tip in contact with the inclined wall. The pipet is kept in contact with the wall for fifteen seconds after free outflow has ceased and is then removed; the water remaining in the tip must not be blown out or otherwise disturbed. From the weight of the water delivered, the capacity of the pipet is calculated, most conveniently by making use of the data in Table LXVIII. If it is not desired to make a new mark, the capacity of the pipet is recorded in the notebook, and a label affixed to indicate the capacity when filled to the mark and allowed to deliver under the conditions described. In all operations involving the use of the calibrated pipet, the corrected volume is used when the calculations are made. At least two checks of the accuracy should be made. If the results of the duplicates differ by more than 0.01 g., the test should be repeated until this degree of concordance is obtained. Varying results point to greasiness of the glass or carelessness in the work.

If it seems desirable to have the pipet deliver exactly the nominal volume, it will be necessary to make a new mark. The internal diameter of the upper stem of the pipet can be measured and the volume corresponding to 1 mm. calculated. Since the error of the pipet has been determined, it is a simple matter to find the position at which the new mark should be placed. A thin strip of gummed paper is used to indicate the new mark, and the pipet is tested as before. If the correct volume is not delivered, it will be necessary to change the position of the mark until the pipet has the designated capacity. Then the new mark can be made permanent by etching a ring into the glass with hydrofluoric acid vapors. For the student the testing of the pipet will suffice.

It should be realized that when pipets are emptied at different temperatures, slightly different amounts of water (or aqueous solution) are left in the pipet, because of the variation of viscosity and surface tension of liquids with temperature. The differences in the amount of water left in the pipet at different laboratory temperatures will, however, be very small and need not be considered if the same conditions of delivery are always fulfilled. When the pipet is used, it must be emptied in exactly the same way as in the calibration or testing.

Burets. A buret is tested at 5 or 10 ml. intervals. The instrument is fixed vertically in a suitable stand and filled slightly above the upper mark. The water should be poured in from a beaker; a wash bottle should not be used. The level of the water is brought to the zero mark by opening the stopcock. The tip of the buret should be examined for air bubbles. If such are found, they must be removed by adding more water and opening the stopcock to its full extent, so that the air will be swept out. It is not necessary to bring the meniscus into exact coincidence with the first graduation; it may be allowed to fall between the 0.00 mark and the 0.10 ml. line, and its position estimated to 0.01 ml. However, it is generally possible so to control the stopcock that the water will flow out very slowly, and then the lower part of the meniscus can be brought into exact coincidence with the first graduation. The accuracy of setting the meniscus to 0.00 is greater than that of estimating the position of the meniscus when it falls between two divisions. In reading the position of the meniscus, it is necessary to avoid parallax by using a reading device (Fig. 108). In the newer burets parallactic errors are very easily avoided by placing the eye so that the front and back of the graduation (next to the meniscus) extending half-way around the tube appear to coincide. The bottom of the meniscus should be made easily visible by the use of the device described on page 521. Before the height of the water is read, it is necessary to be sure that drainage from the upper part of the buret will not alter its level. Since the zero mark is situated a comparatively short distance from the top of the buret, it is sufficient to wait for one minute after filling before reading, to avoid drainage errors. After the reading has been recorded and the tip wiped off to remove adhering water, the stopcock is slowly turned so that the liquid flows out dropwise into a weighed stoppered 100 ml. Erlenmeyer flask (which naturally need not be dry inside). A period of thirty seconds should be required to deliver 5 ml. The level of the water is brought as closely as possible to the 5 ml. mark, although it is not necessary to attain exact coincidence. The tip of the buret is touched to the inside wall of the flask to remove the adhering droplet of water, and the stoppered flask is then weighed to 0.005 g. on the analytical balance. The level of the water is read one-half minute after the end of delivery. Readings are always made to 0.01 ml. by estimation. From the weight of water delivered, the volume delivered is calculated, and the result is compared with the observed volume as obtained by subtracting the first reading from the last. The difference between the observed and calculated values gives the error of the buret at the 5 ml. graduation.

The buret is then filled to the zero mark again and the water allowed to flow out dropwise as before to the 10 ml. mark at a rate not exceeding 10 ml. per minute. The water is received in the same flask, the last weight of which is taken as the initial weight for obtaining the weight of the next portion of water. The meniscus should be read after one-half minute. Continuing in this manner, one tests the buret at 5 or 10 ml. intervals to 50 ml. Each point should be checked twice. Duplicate tests should agree to 0.01 ml., less preferably to 0.02 ml. The data are conveniently recorded as shown in Table LXIX. The manner of obtaining the corrections will be evident from an inspection of the figures in the table. Note that the corrections hold only for a volume of liquid delivered from the zero mark of the buret.

Practical details regarding the use of volumetric apparatus.

Flasks. In making up a solution of definite concentration by weighing out a pure solid and making up to volume, the substance is usually first transferred to a beaker after weighing and dissolved therein. The solution is then transferred quantitatively to the flask, and water is added until the level of the solution has risen nearly to the junction of the flask and the neck, but not into the neck. The flask is now swirled so that the liquid will be mixed fairly well. If this precaution is not taken and water is poured in upon the concentrated solution until the level is nearly at the mark

TABLE LXIX. BURET CALIBRATION

(Temperature = 28.5°)

INTERVAL	WEIGHT OF WATER		TRUE VOLUME	CORRECTION
ml.	g.		ml.	ml.
0.00–10.00	63.89 53.92 9.97	73.86 63.89 9.97	10.02	+ 0.02
0.00–20.00	93.77 73.86 19.91	64.03 44.12 19.91	20.01	+ 0.01
0.00–30.00	93.90 64.03 29.87	74.05 44.17 29.88	30.02	+ 0.02
0.00–40.00	83.96 44.12 39.84	84.07 44.22 39.85	40.04	+ 0.04
0.00–50.00	93.91 44.13 49.78	93.90 44.12 49.78	50.02	+ 0.02

and the final adjustment then made without mixing, it sometimes happens that a contraction or expansion takes place when the concentrated solution is mixed with the water in the final shaking, and the meniscus will no longer fall at the mark. A partial mixing of the solution before making up to the mark will prevent this occurrence. The final adjustment to the mark is made by adding water dropwise from a pipet or a piece of glass tubing. Time must be allowed for water to drain down the sides of the neck if the latter has been wetted; and, of course, drops must not adhere to the inside of the neck above the liquid. If it is intended that the solution shall be made up to the mark at room temperature, it will be necessary, in some cases, to let the solution stand for some time before finally adjusting the meniscus, to equalize the temperature of the solution, which may not be at room temperature because of absorption or evolution of heat resulting from the solution of the substance. It is best, however, to make up to the mark without waiting, to insert the dry stopper carefully, and to mix the solution thoroughly by inverting the flask many times with a simultaneous rotary motion. When the solution is homogeneous, the temperature is taken by immersing a clean dry thermometer in the liquid and reading it to the nearest 0.5°. Solutions should not, as a rule, be stored in volumetric flasks. After the solution has been mixed, it is poured into a dry glass-stoppered bottle. If the stock bottle is not dry, it is rinsed with about three small portions of the solution and drained well after each rinsing. Even if the bottle appears dry, it is best to rinse it once with the solution. The stock bottle is labeled with the name of the reagent, its concentration, the date of preparation, the temperature at which the solution was made up to volume, and the initials of the person who prepared the solution, together with any other pertinent data. The label which appears below is given as an illustration.

Potassium Dichromate

0.1000 *N* (0.01667 *M*)

(2.452 g. recrystallized $K_2Cr_2O_7$ dried at

180° in 500 ml. at 25°)

12–16–33 J. J. L.

Before use the standard solution should be well shaken to mix any condensed water at the top of the bottle with the bulk of the liquid.

Pipets. Unless it is known to be clean, a pipet before use should be rinsed with distilled water, and the latter then allowed to drain out as much as possible. Before the pipet is dipped into the solution, the drop of water remaining in the tip is blown out; and the tip is touched to a clean glass surface or, better, wiped with a piece of filter paper in order that the solution to be pipetted will not be diluted. The pipet is rinsed with two or three small portions of the solution, each portion being brought into contact with the whole inside surface of the pipet before being allowed to run out. The stem of the pipet should not be immersed unnecessarily far into the solution; however, care should be taken that the tip of the pipet does not become uncovered, for then the liquid may be drawn up into the mouth with unpleasant results if it is caustic or poisonous. Strong suction should not be applied. The temperature at which an aliquot portion is removed should be noted. This may be assumed to be the room temperature if the solution has stood for some time in the room; otherwise a thermometer should be used to obtain the temperature.

The pipet must be used in the same way that it was calibrated, i.e., the manner of delivery must be the same, and the same period of drainage must be allowed. It should be understood that when liquids other than water are pipetted, the volumes of liquid then delivered may be considerably different from the volume found in calibration, owing to differences in viscosity, density, and surface tension. Thus a pipet delivering 25.00 ml. of water will not deliver 25.00 ml. of, say, alcoholic potassium hydroxide solution. With dilute ($< 1\ M$) aqueous solutions of salts, acids, and bases, the differences are so small that they may be entirely disregarded. The same considerations apply to the measurements with burets.

It may be said that when a precision of one part in a thousand is required, a pipet smaller than 25 ml. should not be employed, because an error of 0.2 per cent or more can quite easily result from the use of a smaller pipet.

After use, a pipet should be rinsed with distilled water and set in a rack to drain until it is to be used again.

Burets.

Titrations. Before use, a buret is rinsed two or three times with about 5 ml. portions of solution, which is allowed to drain out well each time.[1] The buret is then filled slightly above the mark, the stopcock opened to fill the tip and expel all air, and the level of the liquid brought as closely as possible to the first graduation. Note is made of the temperature. The solution should not be run out too rapidly from the buret during the titration. Apart from the danger of overstepping the end point, the drainage error may then be considerable. The solution should be allowed to flow out rapidly *dropwise* as in the calibration, generally at a rate not exceeding 10 ml. per minute. In making a titration, the stopcock is regulated with the left hand and the stirring rod or flask is held in the right.

The vessels used in titrations may be either beakers or Erlenmeyer flasks. If a beaker is used, a stirring rod must always be employed to mix the liquid. The solution from the buret must not be allowed to accumulate locally in the solution titrated; each drop of reagent as it strikes the liquid in the vessel should be dispersed throughout the whole volume by continuous gentle stirring or swirling. The tip of the buret should not be placed so far above the beaker that splashing results when the added solution strikes the liquid below.

---

[1] In permanent installations burets can be connected directly to the stock bottles (cf. Fig. 113, p. 553).

Erlenmeyer flasks can be highly recommended as titration vessels. No stirring rod is necessary. Efficient mixing is achieved by swirling the flask during the addition of reagent. There is very little danger of loss from splashing, and neither will the evolution of a gas lead to loss. Flasks are very convenient when liquids must be boiled, and their use is demanded when the solution after boiling must be cooled with protection against the air. For example, if a solution is to be made carbon dioxide-free and kept so, it is boiled in a flask with excess of acid and then cooled after inserting a stopper carrying a soda-lime tube. If necessary, carbon dioxide can be excluded from the flask during the titration by passing a stream of carbon dioxide-free air into it (Fig. 109), and in a similar manner titrations can be made in the absence of oxygen by passing in an inert gas (N_2 or CO_2).

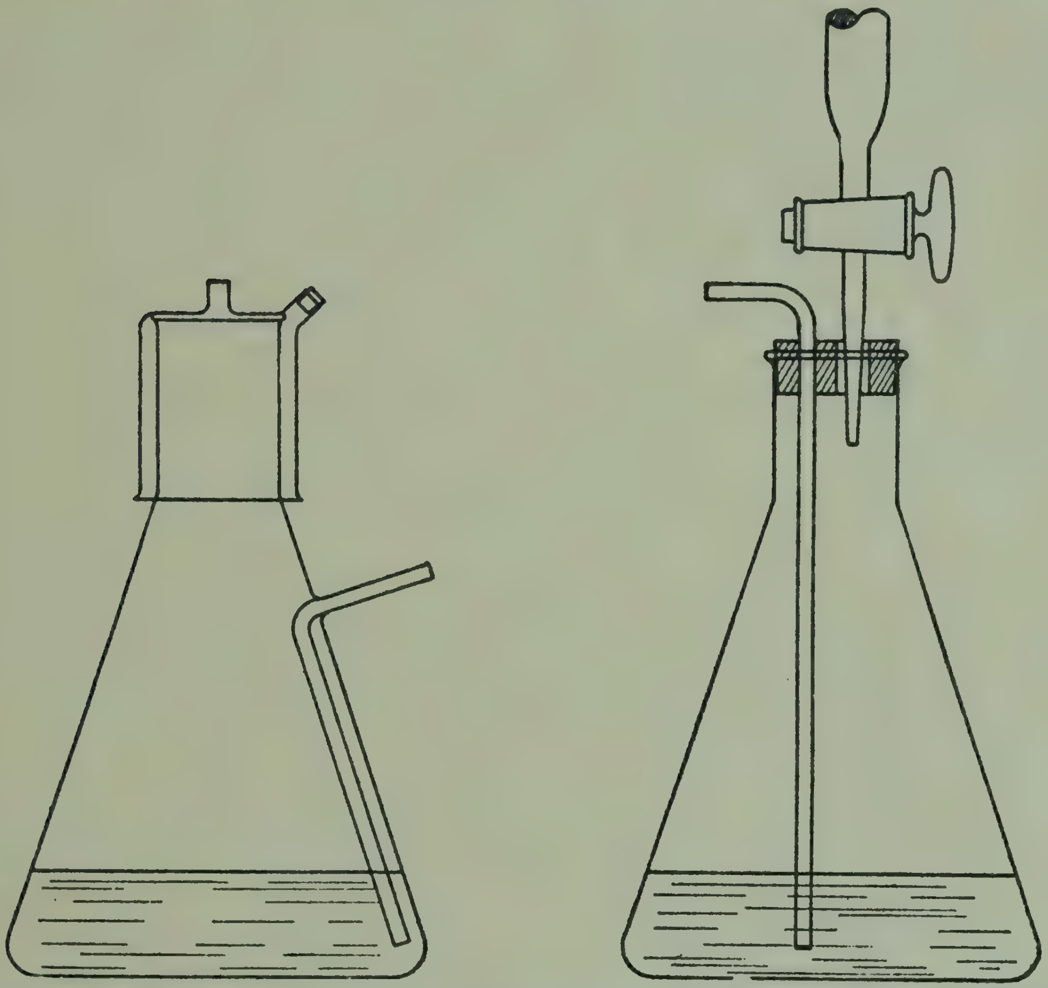


FIG. 109. Apparatus for titration in absence of carbon dioxide or oxygen.

It is a wise plan in any titration, especially if the amount of standard solution required is not known even approximately, to reserve a small portion of the solution to be titrated and to titrate without special care to the end point, running over the latter, perhaps, slightly. The reserved portion can then be added to the main portion and the titration continued carefully to the end point. In this way time can often be saved. The portion reserved should amount to only a few per cent of the whole. Thus, if a sample is dissolved in 50 ml. of solution, about 1 ml. may be removed with a piece of glass tubing and reserved in a small graduate or similar lipped vessel. When the end point has been attained or slightly overstepped, the reserved portion is transferred quantitatively to the titration vessel by rinsing out the graduate and the glass tubing. A special titrating flask (Fig. 110) may also be used.

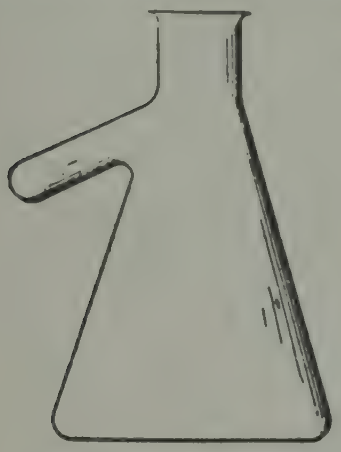


FIG. 110. Titration flask. A portion of the solution to be titrated may be reserved in the side tube.

Near the end point it may be advisable to "split" the drops. The stopcock is slowly turned so that only a fraction of a drop flows out and remains adhering to the tip of the buret. This small volume of liquid may be removed with the stirring rod if a beaker is used, or by touching the tip to the walls of the vessel if a flask is used. In the latter case the flask must be tipped and the liquid carefully swirled so that the droplet will be mixed with the solution. It is best to wash down the sides of the flask with distilled water when near the end point, paying special attention to the upper parts, upon which there may be (but should not be) adhering drops of reagent.

In case it is uncertain whether the end point has been reached or not, the buret should be read, and then another drop added to see whether any distinct change occurs in the solution.

Titrations should be carried out in good light. Direct sunlight is too bright and may cause undesirable chemical changes in the solutions as well (silver titrations with adsorption indicators, some iodometric titrations). Fairly strong indirect daylight is best. Artificial light is often objectionable; certain color changes are very difficult to see by it. "Daylight" or fluorescent lamps, which supply a greater amount of the short wave lengths of the spectrum than do the ordinary, may often be used to advantage.

The solution titrated should generally be viewed against a white background during the titration, and the vessels are therefore placed upon a large porcelain tile, milk-glass plate, or, what is just as effective, a piece of white paper. Color changes will be very easily visible against the light background. In certain titrations in which the end point is indicated by the appearance of a turbidity in the solution, a dark background, such as that supplied by black glazed paper, is best used.

If the color change at the end point is gradual, it is advisable to use a *comparison solution.* The comparison solution should have approximately the same volume and the same composition as the solution titrated at the end point.[1] The amount of indicator added should also be the same in both cases. It will then be very easy to determine the point at which the color of the titrated solution matches that of the comparison solution.

When the titration has been finished, the solution remaining in the buret is allowed to run out (it should not be returned to the stock bottle) unless other titrations are to be made shortly. The buret is then rinsed out with distilled water and covered with an inverted test tube to keep out dust. Solutions should not be allowed to stand for long periods of time in burets, especially if they are of alkaline nature.

Temperature corrections. Due attention must be paid to the matter of corrections for the change in volume of solutions with a change in temperature. In most cases it suffices to assume that the coefficient of cubical expansion of water and dilute solutions (0.1 N and less) is the same and to use the average value, 0.00025 (0.025 per cent) per degree Centigrade, in the interval 20° to 30° when making corrections.[2] The expansion or contraction of the glassware itself rarely needs to be taken into account in practical work, since neglect of this factor introduces an error of only about 0.0025 per cent per degree difference of temperature.

EXAMPLE. One tenth of an equivalent of silver nitrate is dissolved in water and diluted to one liter at 25° in a flask which has been accurately calibrated for 20°. What is the normality of the solution at 25° and at 20°?

Ans.
$$\frac{0.10000}{1.0000 + (5 \times 0.000025)} = 0.09999\ N \text{ at } 25°$$
$$\frac{0.10000}{1.00013 - (5 \times 0.00025)} = 0.10012\ N \text{ at } 20°.$$

Use of special volume burets and weight burets. Measurements of volume of standard solutions delivered with a 50 ml. buret usually cannot be relied upon to less than 0.03 ml. or about 0.1 per cent when the volume is 30 to 40 ml. It may be said then that a titration made with a 50 ml. volume buret can hardly be expected to be closer than 0.1 per cent to the theoretical value, assuming that the other operations have been carried out without any error at all. If an accuracy greater than this is desired in a volumetric procedure, it will be necessary to make more refined measurements of the amount of the standard solution. There are two ways of proceeding. The first method involves the use of a special buret, sometimes called a chamber buret (Fig. 111), in which the middle portion is quite wide but to which there are attached rather narrow tubes, above and below. The upper tube bears a single graduation, which is the zero mark. The tube below the central enlarged portion is graduated like an ordinary buret into ml. and fractions of a ml. The distance between the marks may be 0.01 ml., in which case it will then be possible to estimate to 0.001 ml. The volume of the graduated portion of the buret may amount to only 5 or 10 ml., the total volume of the buret being perhaps 50 to 100 ml. Titrations can then be made with a precision approaching 0.01 per cent as far as the measurement of volume is concerned. It is, of course, necessary when using a buret of this kind to take a weight of sample such that when the titration is completed the meniscus will be in the graduated portion of the vessel. If the approximate content of the desired constituent in the sample is not known, a preliminary titration must be run using an ordinary buret. When using an instrument of this kind, great care must be taken to avoid errors of drainage and of change of volume due to temperature variations.

---

[1] Thus in standardizing hydrochloric acid by titrating against borax. $Na_2B\,O_7 \cdot 10\,H_2O$, using bromcresol green as indicator, the comparison solution is prepared by dissolving the correct amounts of sodium chloride and boric acid in water together with the indicator.

[2] Thus water has the relative volumes 1.0000, 1.0011, and 1.0025 at 20°, 25°, and 30°, respectively, while 0.1 M hydrochloric acid has the relative volumes 1.0000, 1.0012, and 1.0026 at the same temperatures; and similar figures are obtained for most other solutions of comparable concentration.

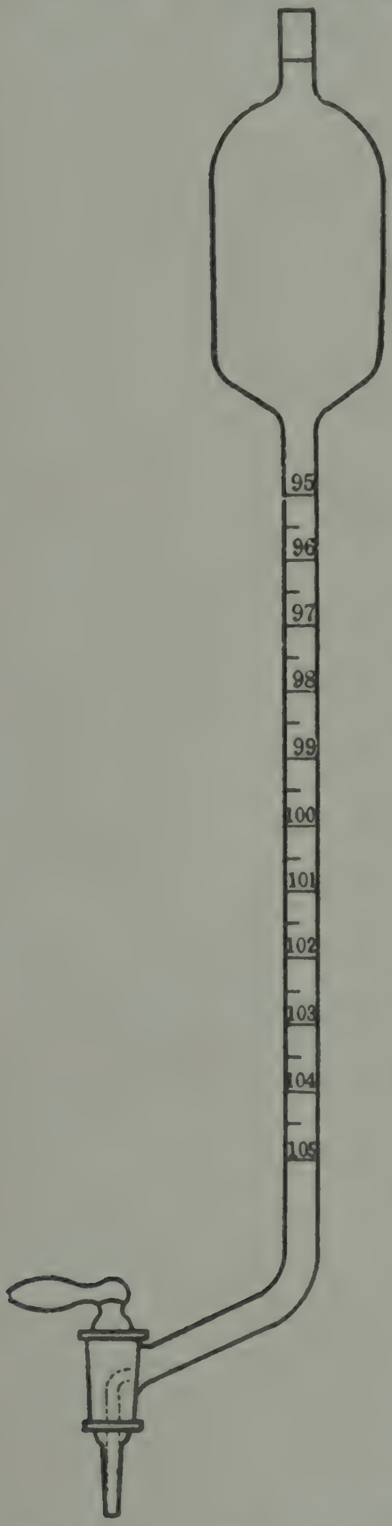


FIG. 111. Chamber buret.

The second and better method of accurate determination of the amount of standard solution used in a titration is based on the *weighing* of the solution. The vessel used is called a weight buret (Fig. 112). It may have a volume of 50 or 100 ml. and is roughly graduated. It is weighed before and after a titration, and the amount of reagent is then calculated from the weight added, the solution having been standardized on the weight basis. The concentration of the solution is expressed in terms of the number of moles or equivalents in 1000 g. of solution instead of 1000 ml. Since the weight of the solution delivered can be determined with great precision, the use of a weight buret leads to very precise results as far as the measurement of the amount of standard solution is concerned. It is impossible to measure 40 ml. of solution from a buret with an accuracy of 0.01 ml., whereas it is not difficult at all to weigh the solution with an accuracy of 0.01 g. Generally it is more than sufficient to weigh the solution to the nearest 1 mg. This would correspond to a precision of 0.002 per cent in a weight of 50 g. Errors from drainage, change in temperature, etc. are entirely eliminated when weight burets are used.

The use of a weight buret or a special volume buret is of value only when the other steps of the procedure can be carried out with a precision that is comparable to that of the measurement of the amount of standard solution. In the first place, it must be possible to locate the position of the end point with great precision by a sharp change in color of the indicator or otherwise. Then it is necessary to be able to add very small increments of solution near the end point. If the end point were overstepped 0.01 ml. by the inability to add a smaller amount than this volume, it would be illogical to weigh to 0.001 g. Since it is difficult to add portions of liquid smaller than 0.01 ml., it is often necessary to titrate in a special manner near the end point. The end point may be intentionally slightly overstepped and the excess of reagent then determined by titrating back with a very dilute solution — say 0.001 N — of an appropriate substance; or the addition of the titrating solution in the weight buret may be stopped shortly before the end point and the titration continued by adding a solution one tenth as strong. The measurement of volume of the dilute solution can be made with an ordinary buret.

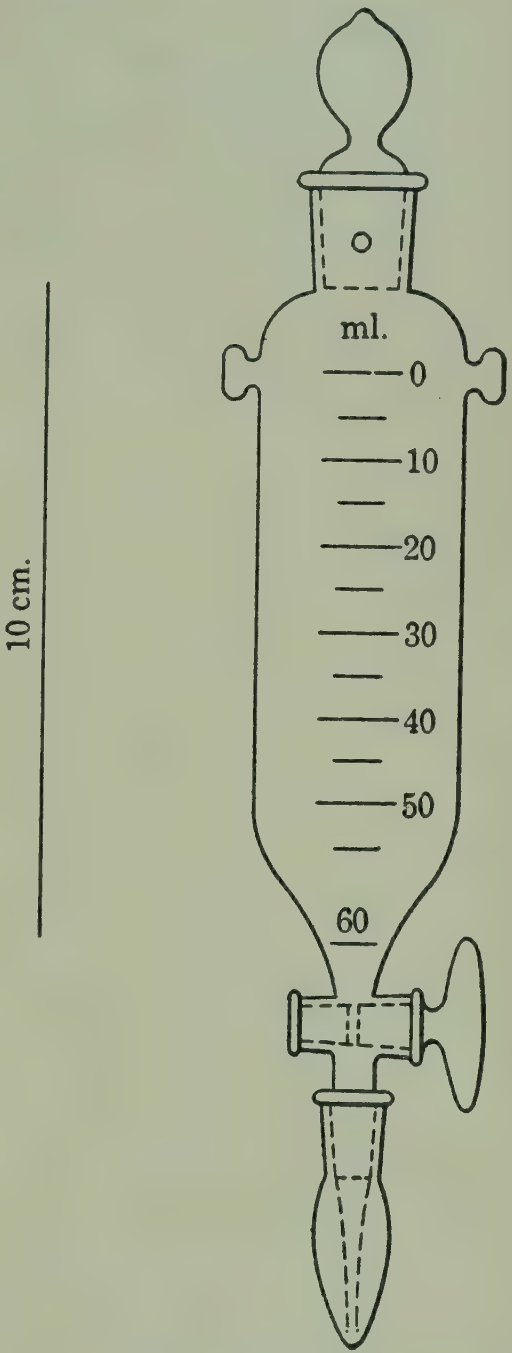


FIG. 112. Weight buret according to La Mer and Friedman (Ind. Eng. Chem., Anal. Ed. *2*, 54 (1930)).

PROBLEMS

1. A volumetric flask filled to the mark holds 997.00 g. of water at 21.5°. What is its volume at 20°; at 21.5°?
Ans. 1000.10 ml. at 20°, 1000.14 ml. at 21.5°.

2. A pipet delivers 49.90 g. of water at 23°. What is its volume?
Ans. 50.07 ml. at 20°.

3. A solution of hydrochloric acid is found to be 0.10055 N at 22°. What will be its normality at 28°?
Ans. 0.10040 N.

4. What will be the capacity of a flask at 30° which was found to hold 997.18 g. of water at 20° if the cubical coefficient of expansion of the glass is 0.000015 per degree Centigrade?

5. What actual mass of water does a correctly marked liter flask hold at 20°?

6. What weight of water must be taken at 25° to indicate the mark that will represent a volume of 1 liter at the same temperature?

7. If a volumetric flask is to be calibrated at 20° with an accuracy of 0.01 per cent, what is the greatest permissible error in obtaining the temperature of the water?

8. 5.8110 g. of sodium chloride are transferred to a liter flask, dissolved in water, and the solution made up to the mark at 23°. The mark on the flask has been found to correspond to a volume of 1000.48 ml. at 20°. What is the molarity of the solution? If 50.00 ml. of the solution are pipetted out at 28°, what weight of sodium chloride will be taken?

9. What weight of a liquid having a density of 0.8986 at 20° and a cubical coefficient of expansion of 0.030 per degree Centigrade in the neighborhood of 20° must be taken to indicate a volume of 500.0 ml. in a glass vessel at 25°?

VOLUMETRIC DETERMINATIONS

CHAPTER XXXIV

ACIDIMETRY AND ALKALIMETRY

Standard hydrochloric acid.

The strong inorganic acids are commercially available in the form of concentrated solutions. The specific gravities of solutions of acids and bases of various concentrations can be found in handbooks.[1] Therefore if the commercial product is pure, its strength can be found by the careful determination of the specific gravity, and a standard solution can be prepared by proper dilution. It is necessary, however, not to rely entirely upon the empirical tables giving the relation between concentration and specific gravity but to determine the normality of the acid after dilution.

Solutions of hydrochloric acid are entirely satisfactory as standard solutions for alkalimetric titrations. In many laboratories standard sulfuric acid is preferred, especially for titrations of hot liquids or when the substance to be determined must be boiled for some time with an excess of acid. In many of these cases hydrochloric acid may be used as well. For example, 0.1 N hydrochloric acid may be boiled for an hour without loss of a trace of acid, if the evaporated water is continually replaced. Even 0.5 N hydrochloric acid may be boiled for about ten minutes without any loss of acid.

Hulett and Bonner [2] have recommended a *constant-boiling* mixture of hydrochloric acid and water for the preparation of standard solutions. The vapor of the constant-boiling acid has the same composition as the liquid. The concentration of this constant-boiling mixture depends upon the pressure under which it is distilled. To prepare the constant-boiling acid, Foulk and Hollingsworth [3] start with a hydrochloric acid solution of specific gravity 1.18 and distill with a speed of 3–4 ml. per minute. After about three fourths of the original liquid has been distilled and rejected, the constant-boiling mixture is collected in a dry flask. It is best to begin with a liter or more of acid. The distillation is discontinued when a residue of only 50–60 ml. remains in the distilling flask. The barometric pressure during the distillation should be read to 1 mm. The "equivalent weight" of the acid is given in the following table. The constant-boiling mixture can be kept in well-closed bottles without change.

---

[1] Compare I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis*, Vol. II.

[2] G. A Hulett and W. D. Bonner, J. Am Chem. Soc. *31*, 390 (1909). See also W. D. Bonner and A. C. Titus, *ibid. 52*, 633 (1930); Titus and D. E. Smith, *ibid. 63*, 3266 (1941).

[3] C. W. Foulk and M. Hollingsworth, J. Am. Chem. Soc. *45*, 1223 (1923).

TABLE LXX. COMPOSITION OF CONSTANT-BOILING HYDROCHLORIC ACID

ATMOSPHERIC PRESSURE DURING DISTILLATION IN MM. OF MERCURY	CONCENTRATION OF HYDROCHLORIC ACID IN GRAMS OF HCl PER 100 GRAMS (REFERRED TO VACUUM)	WEIGHT OF DISTILLATE CONTAINING ONE MOLE OF HCl, WHEN WEIGHED IN AIR
780	20.173	180.621
770	20.197	180.407
760	20.221	180.193
750	20.245	179.979
740	20.269	179.766
730	20.293	179.551

Preparation of 1 N hydrochloric acid. Follow (a) or (b).

(a) Weigh a dry stoppered 250 ml. Erlenmeyer flask to 0.01 g. Introduce the approximate amount of *constant-boiling acid* required for half a liter of 1 *N* solution. Care must be taken to avoid wetting the neck of the flask. Reweigh the flask to 0.01 g., after replacing the stopper. Then add 100 ml. of water (which is in equilibrium with the air), and transfer the contents quantitatively to a 500 ml. volumetric flask. Dilute to the mark after the solution has attained room temperature, stopper, and mix. Transfer the acid to a dry glass-stoppered bottle, and label with the date of preparation and the normality.

(b) If no constant-boiling mixture is available, a C. P. product of approximately known specific gravity can be taken. Measure with a graduate as carefully as possible the proper volume of the concentrated acid (12 *N*), and dilute as described above.

Preparation of 0.1 N hydrochloric acid. 0.1 *N* hydrochloric acid may be prepared by diluting the constant-boiling mixture or the concentrated acid. For the present purpose it may be obtained from the 1 *N* acid by taking two 50 ml. portions of the latter with a pipet and diluting in a volumetric flask to 1 liter. Transfer the diluted solution to a glass-stoppered liter bottle. Standardize as described below, and label.

Preparation of 0.01 N hydrochloric acid. Dilute two 50 ml. portions of the 0.1 *N* acid in a volumetric flask to 1 liter.

Standardization of 0.1 *N* hydrochloric acid. Sodium carbonate as standard substance.

Preparation of anhydrous sodium carbonate. Analytical-grade sodium bicarbonate, which ordinarily is contaminated with a small amount of carbonate, is suitable for the preparation of pure anhydrous sodium carbonate.[1] About 10 g. of the pure bicarbonate are placed in a porcelain or, better, a platinum crucible and pressed against the walls of the crucible with a spatula to form a uniformly thick layer. The crucible is then heated in an air bath (a double-crucible arrangement with asbestos plate, p. 184) or, better, in an electric furnace for one hour at a temperature between 270° and 300°. The contents are preferably stirred occasionally during the heating. After removal from the furnace the crucible is allowed to cool in a desiccator. By heating to 270°–300°, the sodium bicarbonate is quantitatively changed into the carbonate. If the temperature rises much above 300°, there is danger that sodium carbonate will lose carbon dioxide. The carbonate will absorb water if exposed to the atmosphere and form the monohydrate (p. 129); therefore the anhydrous salt should be kept in a bottle with a well-fitting stopper.

Instead of preparing sodium carbonate from the bicarbonate, an analytical-grade sodium carbonate can be used after drying for one half to one hour at 270° to 300°. The final product should be tested for purity.

Chloride. A solution of 0.5 g. of sodium carbonate in 10 ml. of 2 *N* chloride-free nitric acid must give with silver nitrate either no opalescence or only a very slight one that is no stronger than that obtained with 10 ml. of a solution containing 5 mg. of sodium chloride per liter of 1 *N* nitric acid, when treated with silver nitrate. Sensitivity, 0.01 per cent NaCl in Na_2CO_3.

Sulfate. A solution of 0.5 g. of sodium carbonate in 10 ml. of 2 *N* acetic acid should give no turbidity or separation of barium sulfate with barium nitrate after standing for fifteen minutes. Sensitivity, 0.01 per cent Na_2SO_4.

Potassium. A solution of 0.5 g. of sodium carbonate in 10 ml. of 2 *N* acetic acid should not show a turbidity after standing for five minutes after addition of 1 ml. of sodium cobaltinitrite solution (de Koninck's reagent) and 10 ml. of alcohol. Sensitivity, 0.04 per cent K_2CO_3.

Sodium hydroxide. 30 ml. of water are boiled for two minutes in a Pyrex flask, 2 g. of sodium carbonate are then added, and a soda-lime tube is attached to the vessel after it is removed from the flame. Immediately after the carbonate has dissolved, 25 ml. of 20 per cent barium chloride are added to the hot solution, which is then shaken and cooled with the soda-lime tube in place; 2 drops of 1 per cent phenolphthalein are added. After cooling, the liquid (if colored) should not require more than 0.1 ml. of 0.01 *N* acid for decolorization. Sensitivity, 0.04 per cent NaOH.

Water and sodium bicarbonate. 10 g. of sodium carbonate are quickly weighed into a covered platinum crucible; the latter is heated for one hour at 300° and rapidly weighed after cooling. The loss in weight should not amount to more than 1 mg.

Insoluble substances. The solution of 5 g. of sodium carbonate in 25 ml. of water must be entirely clear.

---

[1] Very pure sodium bicarbonate can be prepared from C. P. sodium carbonate by saturating a strong solution of the latter with carbon dioxide to precipitate the bicarbonate

Procedure for standardization. Weigh out 0.2 to 0.25 g. of sodium carbonate accurately, transfer to a 250 ml. Pyrex flask, and dissolve in 25 ml. of water. Add one drop of phenolphthalein solution (p. 449), and titrate with the 0.1 *N* hydrochloric acid to be standardized until the solution is colorless. At this point the sodium carbonate will have been transformed into bicarbonate with a little acid present in excess. Therefore somewhat less than the volume of acid used up to this point must be added to transform all the carbonate into carbon dioxide (cf. Fig. 82 and pp. 461, 558):

$$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$$
$$NaHCO_3 + HCl \rightarrow H_2O + CO_2 + NaCl.$$

Add a few drops of bromcresol green, and continue the titration until the color of the indicator begins to change from blue to green. At this point the solution still contains a trace of sodium bicarbonate and a large amount of carbon dioxide. Remove the latter by boiling the solution for one to two minutes, during which time the color changes to blue and finally to violet (mixed color of blue of bromcresol green and red of phenolphthalein). Cool the solution to room temperature, and continue the titration until the color changes to green. Repeat the procedure with two other portions of sodium carbonate. Calculate the normality of the acid.

NOTES:

1. Methyl yellow, methyl orange, the mixed indicator methyl orange with indigo carmine (see p. 450), or bromphenol blue may be used as indicators instead of bromcresol green. With the first three indicators the solution should be cooled to room temperature after boiling, before continuing the titration to the end point.

2. Just before the equivalence point is reached, the solution is supersaturated with carbon dioxide. This explains why the first color change on titrating at room temperature is reached a trifle too early. If, after reaching the first color change at room temperature, the solution is boiled, the excess of carbon dioxide is expelled; and a sharp end point is obtained thereafter. The indicator blank can be determined by taking an equal volume of water containing approximately the same amounts of sodium chloride and indicator as are present in the solution titrated at the end point and adding hydrochloric acid until the color of the blank is equal to that of the solution at the end point.

3. No indicator correction is found if phenol red, bromthymol blue, or methyl red is used as indicator. The titration must then be carried out at boiling temperature, and hydrochloric acid added until the acid color of the indicator does not turn alkaline upon continued boiling. This procedure is recommended for the standardization of 0.01 *N* or more dilute acid. It is

advisable to determine in a preliminary trial the approximate amount of acid required for reaching the end point, then to add in the standardization a little less than this amount, to boil five minutes, and finally to continue the titration in the manner described above. It is still simpler to reserve a small volume of the solution titrated, which is then added to the main portion when the end point in the latter has been reached (see p. 540).

4. Any of the indicators having a color-change interval located between those of phenolphthalein and methyl orange can be used if a slight excess of hydrochloric acid is added, the solution is boiled for five minutes or heated on a steam bath for half an hour to remove all carbon dioxide, and the excess of acid is finally back-titrated with 0.01 *N* sodium hydroxide.

5. In the standardization of 0.5 *N* or stronger acids with methyl orange, methyl yellow, or bromphenol blue as indicator, the titration can be carried out at room temperature directly to the end point; the end point is reached when the color of the solution becomes orange-red or yellow-purple respectively. It is recommended that the solution be shaken vigorously just before the end point is reached, in order to remove that part of the carbon dioxide which is present in supersaturated solution.

6. Hydrochloric acid can be standardized gravimetrically by precipitation as silver chloride. This is one of the most exact methods for standardizing the acid, if the weight of the silver chloride is large enough to make the weighing errors negligibly small.

Other standard substances.

Various standard substances can be used in place of sodium carbonate for the standardization of strong acids. A description of the preparation and purity test of these standards is given by Kolthoff and Stenger in *Volumetric Analysis*, Vol. II. For details the student is referred to this text.

Borax, $Na_2B_4O_7 \cdot 10\ H_2O$. Sodium tetraborate decahydrate is obtained in a pure condition by two recrystallizations of a good product from water, followed by drying to constant weight in a desiccator over a solution saturated with respect to sucrose and sodium chloride.[1] Hurley[2] showed that the recrystallized salt can be obtained quickly in the dry state by washing it with alcohol and ether and sucking it air-dry. It should be kept in well-closed bottles, or else it may lose water and effloresce to the pentahydrate. Borax has the advantage of a large equivalent weight (190.71; that of sodium carbonate is 52.98), and the standardization can be carried out at room temperature with methyl red as indicator. The indicator blank is negligibly small. Its use as a standard substance is highly recommended.

Sodium oxalate, $Na_2C_2O_4$. This substance was originally recommended by Sörensen[3] as an ideal primary standard. It is easily obtained in a pure state and can be converted by heating at the proper temperature into sodium carbonate, in which form it is used for standardizing acids:

$$Na_2C_2O_4 \rightarrow Na_2CO_3 + CO.$$

---

[1] H. Menzel, Z. anorg. allgem. Chem. *224*, 10 (1935).

[2] F. H. Hurley, Ind. Eng. Chem., Anal. Ed. *8*, 220 (1936); *9*, 237 (1937).

[3] S. P. L. Sörensen, Z. anal. Chem. *36*, 639 (1897); *42*, 333, 512 (1903); *44*, 156 (1905); *45*, 217 (1906).

Sodium oxalate is also very useful in the standardization of potassium permanganate (p. 592).

Potassium bicarbonate, $KHCO_3$. This substance can be obtained in a pure state by recrystallization from aqueous solutions in the presence of carbon dioxide or by precipitation with alcohol. Its equivalent weight is almost twice that of sodium carbonate.

Calcite, calcium carbonate (Iceland spar). Calcite, in the form of Iceland spar, is not pure enough to warrant its use as a standard substance. Moreover, in the standardization against calcium carbonate, an excess of acid must be added to dissolve all of the carbonate, and a back-titration is unavoidable; this procedure is not conducive to accuracy.

Potassium bitartrate. By ignition this substance is converted into potassium carbonate, which can be used for the standardization of acids.

Potassium iodate. Potassium iodate may be used for the direct standardization of acids by making use of the reaction:

$$IO_3^- + 5\,I^- + 6\,H^+ \rightarrow 3\,I_2 + 3\,H_2O.$$

By adding an excess of neutral alkali iodide and sodium thiosulfate to a solution of potassium iodate, hydrogen ions are removed upon addition of hydrochloric acid, until all of the iodate has been converted into iodine. The iodine is removed by the excess sodium thiosulfate:

$$2\,Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2\,NaI.$$

Therefore the liquid remains neutral and colorless during the titration with hydrochloric acid until the end point is reached. As soon as all of the iodate has been used up, the solution becomes acid, as indicated by the color change of methyl yellow, methyl orange, bromcresol green, etc.

Mercuric oxide, HgO. Mercuric oxide has a high equivalent weight and can be kept unchanged. It contains no water of crystallization, and it is not hygroscopic. Acid solutions can be standardized against this substance by using phenolphthalein or methyl yellow as indicator. In the standardization use is made of the fact that mercuric oxide dissolves in potassium iodide with the formation of potassium mercuric iodide and an equivalent amount of potassium hydroxide:

$$HgO + 4\,KI + H_2O \rightarrow K_2HgI_4 + 2\,KOH$$

$$\text{(or}\quad HgO + 4\,I^- + H_2O \rightarrow HgI_4^= + 2\,OH^-).$$

The colorless solution is titrated with acid, using an indicator with a color-change interval between pH 8 and 4. Instead of potassium iodide, much potassium bromide or sodium thiosulfate may be used.

Preparation of standard alkali.

The hydroxides of sodium, potassium, and barium are used in the preparation of solutions of standard base; of these, sodium hydroxide is the most generally used. Most analytical grades of the latter reagent contain small amounts of sulfate, chloride, and silica, besides smaller or larger amounts of water and carbonate. Therefore a standard solution cannot be prepared by dissolving an exactly weighed amount in a certain volume of water. Moreover, it is desirable in most cases to have carbonate-free standard base available. If barium hydroxide is used as the base, carbonate need not be removed from the solution by the addition of any special reagent, since barium carbonate is insoluble in barium hydroxide solution. Therefore in the preparation of a solution of this base the precipitate is allowed to settle, and the supernatant liquid is siphoned off with protection against the atmosphere to exclude carbon dioxide.

Various methods are used for the preparation of carbonate-free sodium hydroxide. If for certain purposes (for example, in physicochemical research) it is desirable to have the base solution free of all impurities, it can be prepared by converting metallic sodium into sodium hydroxide (*Care! Explosion!*). Sodium and potassium hydroxides purified by treatment with alcohol are commercially available in the form of pellets which do not contain an appreciable amount of impurities, except some water and a little sodium carbonate. Solutions prepared from these purified products can be used for many analytical purposes.

Carbonate can be removed from sodium hydroxide solutions by the addition of an excess of barium or strontium chloride. The resulting solution of the base then contains barium or strontium ions; therefore instead of applying this purification process, one might as well, in many cases, substitute barium hydroxide for sodium hydroxide. In general, however, the use of sodium hydroxide is to be preferred, since barium may give precipitates which are objectionable because of coprecipitation of hydroxide (in the titration of sulfuric acid, for example).

In the preparation of carbonate-free sodium hydroxide, use is also made of the fact that sodium carbonate is insoluble in a concentrated solution of sodium hydroxide.

Procedure for the preparation of concentrated carbonate-free sodium hydroxide. Dissolve 50 g. of C. P. sodium hydroxide in 50 ml. of water in a Pyrex flask. The sodium carbonate remains in suspension after the base has dissolved and settles very slowly. Therefore filter the strong lye through a Gooch or sintered-glass crucible with exclusion of air to prevent contamination by atmospheric carbon dioxide. If a centrifuge is available, a clear carbonate-free solution may be obtained by centrifuging for a short time. The strong carbonate-free sodium hydroxide solution can be kept in paraffin-lined or ceresine-lined glass bottles.

The above method cannot be applied to the preparation of carbonate-free potassium hydroxide, because potassium carbonate is appreciably soluble in the concentrated base solution. In this case the lime method[1] is recommended for the preparation of a practically carbonate-free solution.

Preparation of standard sodium hydroxide solutions.

Water for diluting. The water used for the dilutions should not contain an excess of carbon dioxide. Ordinary distilled water is often supersaturated with carbon dioxide. The excess can be removed either by boiling the water for a few minutes and cooling, or by drawing air, washed by acid and water, through it for some hours. Water in equilibrium with the atmosphere is 1.5×10^{-5} molar with respect to carbon dioxide. If 0.01 *N* sodium hydroxide is prepared by diluting carbonate-free 0.1 *N* sodium hydroxide with this equilibrium water, only 0.3 per cent of carbonate is introduced. Water can be tested in the following way for the presence of an excess of carbon dioxide: 500 ml. of the water treated with 5 drops of 1 per cent phenolphthalein solution should not require more than 0.3 ml. of 0.1 *N* alkali to give a permanent red color.

Storing of standard alkali. Solutions of strong bases absorb carbon dioxide from the air; if alkali hydroxides are exposed to the atmosphere, they rapidly become contaminated with carbonate; barium hydroxide solutions become turbid owing to formation of insoluble barium carbonate. Short exposure of an alkali hydroxide solution to the atmosphere is not very harmful, at least when the temperature of the solution does not differ much from that of the surrounding air. When the standard solutions are quickly transferred to a buret, the contamination by carbon dioxide can be disregarded. However, the solution in the buret should be protected from the atmosphere by a soda-lime tube.

In general it is recommended that the burets be connected with the stock bottles in such a way that contamination by carbon dioxide is eliminated. An arrangement such as that shown in Figure 113 serves the purpose quite well and is recommended for more permanent installations.

Sodium hydroxide is tested for carbonate by filling a test tube to within 2 cm. of the top with the solution and adding 1 ml. 0.5 *N* barium chloride. The tube is immediately stoppered and the contents mixed. No turbidity should appear. It is desirable to make this test at various times after the standard solution has been prepared.

When strongly alkaline solutions are kept in ordinary glass vessels, they become contaminated with silicates owing to the attack of the glass. Solutions of barium hydroxide will form a white deposit, since barium silicate is insoluble. Therefore it is quite generally recommended that the standard alkali be kept in paraffined containers.[1]

---

[1] I. M. Kolthoff, Z. anal. Chem. *61*, 48 (1922).

Preparation of approximately 1 N sodium hydroxide. Weigh out approximately 40 g. of the concentrated carbonate-free sodium hydroxide solution into a 100 ml. Erlenmeyer flask, transfer to a volumetric flask of 500 ml., make up to the mark with equilibrium water, and mix well. Transfer to a clean rubber-stoppered bottle, and label. Do not expose the solution to the air longer than is strictly necessary.

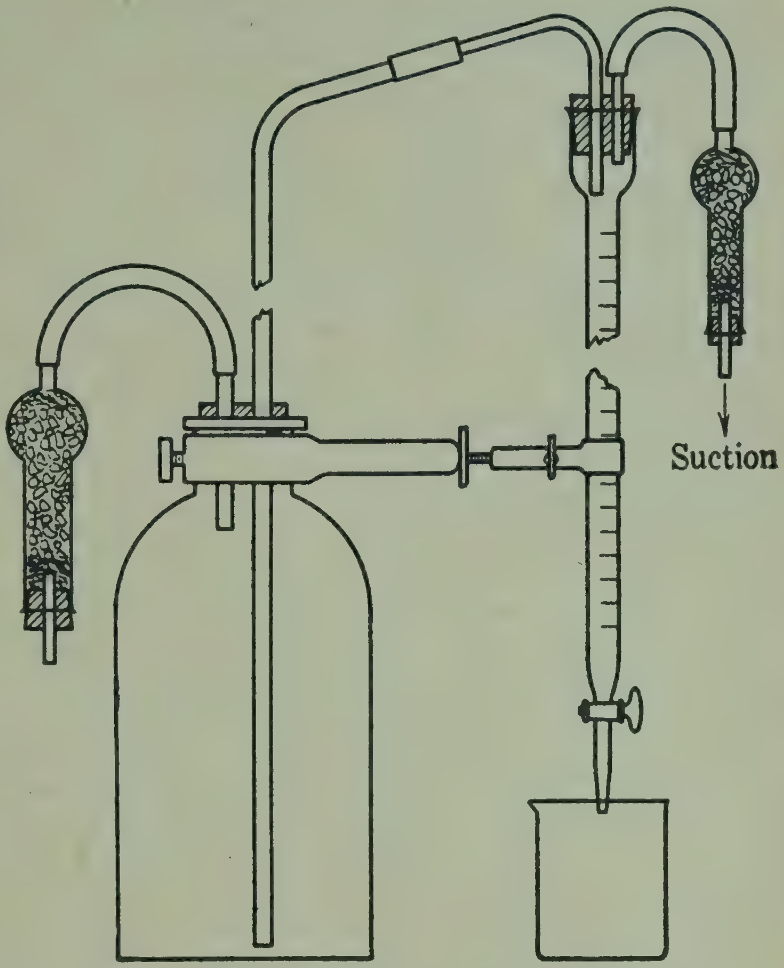


FIG. 113. Arrangement for protection of standard base against carbon dioxide.

Preparation of approximately 0.1 N sodium hydroxide. Pipet two 50 ml. portions of the approximately 1 *N* sodium hydroxide solution into a 1 liter volumetric flask, and dilute with equilibrium water to the mark. Transfer the solution, after thorough mixing, to a dry bottle and keep tightly stoppered. Standardize as described below.

Preparation of approximately 0.01 N sodium hydroxide. Pipet 50 ml. of the 0.1 *N* solution into a 500 ml. volumetric flask, and dilute to the mark with equilibrium water.

Standardization of 0.1 *N* sodium hydroxide. Potassium biphthalate as standard substance. $C_6H_4(COOH)COOK$.

Potassium biphthalate is obtained as a 99.97 per cent pure product from the Bureau of Standards. A C. P. product can be purified by recrystallization from water after the addition of enough potassium carbonate to ensure the absence of free phthalic acid, followed by recrystallization from pure water. The crystals should separate at a temperature above 30°. They are collected, washed, and dried at 125°. The salt is not hygroscopic and can be kept unchanged.

---

[1] B. A. Soule, Ind. Eng. Chem., Anal. Ed. *1*, 109 (1929), has shown that a coat of thermoprene, a rubber paint made by the B. F. Goodrich Company, Akron, Ohio, is very good for preventing alkaline solutions from attacking glass.

Procedure for the standardization. Weigh out three 0.8 to 0.9 g. portions of the salt into 250 ml. Pyrex flasks and dissolve in 25 ml. of equilibrium water. Titrate each solution with the base to be standardized, using phenolphthalein or thymol blue as indicator. If the alkali solution is carbonate-free, a sharp color change is obtained which is permanent for at least five minutes. Calculate the normality.

Other standard substances.

Benzoic acid, C_6H_5COOH. Pure benzoic acid can be obtained from the Bureau of Standards. The substance is very voluminous and contains hygroscopic water. It is therefore melted by heating to a temperature of 130° to 140° and poured into a platinum dish; after cooling, the cake is ground up in an agate mortar. The acid is only slightly soluble in water but is very soluble in alcohol. Weighed portions of the acid are dissolved in 20 ml. of alcohol which has been previously neutralized to phenolphthalein with alkali. The solution is then titrated with the solution to be standardized, using the same indicator.

Crystallized oxalic acid, $(COOH)_2 \cdot 2\,H_2O$. The C. P. acid is recrystallized by dissolving 500 g. in an equal quantity of boiling 3 to 4 *N* hydrochloric acid, filtering, and cooling with stirring. Calcium is removed in this way. The crystal meal is transferred to a Büchner funnel with a sintered-glass bottom; and after removal of the mother liquor by suction, the crystals are washed several times with dilute hydrochloric acid. The product is then recrystallized from water until chloride-free. The final crystals are quite pure but can contain as much as 0.2 per cent of occluded water. In order to remove this water, the crystals are dehydrated in a desiccator over sulfuric acid at 60°. The oxalic acid loses its water of crystallization, and the crystals break down to a very fine powder; and therefore the vacuole water is lost. The fine powder is then rehydrated by exposing it to the air or by keeping it in a desiccator over deliquescent sodium bromide until the weight is constant. The final product does not contain more than 0.01 per cent of hygroscopic water and is stable at relative humidities between 5 and 95 per cent. About 0.25 g. of the acid is dissolved in equilibrium water and titrated with the standard base, phenolphthalein or thymol blue being used as indicator.

Potassium bi-iodate, $KH(IO_3)_2$. Potassium bi-iodate possesses many advantages as a primary standard. Since iodic acid is a strong acid, the standardization can be made with any indicator showing a color change between pH 4 and 10. The salt has a high equivalent weight. It is anhydrous, nonhygroscopic, and can be kept unaltered.

Potassium bitartrate, $COOH \cdot CHOH \cdot CHOH \cdot COOK$. This salt is only slightly soluble in cold water but easily soluble at higher temperatures. A weighed portion of the pure salt is dissolved in warm water and titrated with standard base (phenolphthalein as indicator).

Hydrazine sulfate, $N_2H_4 \cdot H_2SO_4$. This substance is anhydrous and can be obtained in a pure state by recrystallization from water and drying at 150°. In the standardization methyl red is used as indicator:

$$2(N_2H_4 \cdot H_2SO_4) + 2\ NaOH \rightarrow (N_2H_4)_2 \cdot H_2SO_4 + Na_2SO_4 + 2\ H_2O.$$

EXERCISES

Titrate 25 ml. of standard 1 *N*, 0.1 *N*, and 0.01 *N* hydrochloric acid with standard 1 *N*, 0.1 *N*, and 0.01 *N* sodium hydroxide respectively, using methyl orange (or methyl yellow, or bromphenol blue), methyl red, phenol red (or bromthymol blue), and phenolphthalein (or thymol blue) as indicators. Make the same titrations by adding the acid to the base. Report the results as follows:

TITRATION OF ACID WITH STANDARD BASE

INDICATOR	COLOR AT END POINT	ML. 1 *N* ALKALI REQUIRED	CALCULATED ML.	ML. 0.1 *N* ALKALI REQUIRED	CALCULATED ML.	ML. 0.01 *N* ALKALI REQUIRED	CALCULATED ML.
Methyl orange							
Methyl red							
Phenol red							
Phenolphthalein							

TITRATION OF BASE WITH STANDARD ACID

INDICATOR	COLOR AT END POINT	ML. 1 *N* ACID REQUIRED	CALCULATED ML.	ML. 0.1 *N* ACID REQUIRED	CALCULATED ML.	ML. 0.01 *N* ACID REQUIRED	CALCULATED ML.
Methyl orange							
Methyl red							
Phenol red							
Phenolphthalein							

1. The acid and the base were both standardized independently. Does the amount of base required in the titration of 25 ml. of acid correspond to the calculated amount?

2. Interpret the results in those cases in which the amounts found and calculated do not agree. Consider the excess of acid or base present at the end point, and calculate the correction for the indicator blank (see Table LVIII, p. 448).

If the alkali solution is titrated with acid, the former is exposed to the air for a longer or shorter period and will absorb some carbon dioxide. Explain what influence a possible carbonate content will have on the results obtained with the various indicators.

Titration of a weak acid.

Determination of the strength of glacial acetic acid. Weigh a dry stoppered 50 ml. flask, introduce 2 to 2.5 g. of the acid, and reweigh, taking care that the acid does not touch the neck of the flask. After the weight has been determined, add 20 to 30 ml. of water and transfer the solution quantitatively to a 500 ml. volumetric flask. Make up to the mark with equilibrium water. After thorough mixing, titrate 25 ml. portions of the acid with 0.1 *N* standard base, using the following indicators: methyl orange, methyl red, phenol red, and phenolphthalein.

1. Which indicator changes color sharply at the end point?
2. Explain why the unsuitable indicators give vague color changes, and indicate how large the errors may be with different indicators.
3. Calculate the acetic acid content of the sample titrated.
4. How many equivalents of acid does the sample contain per gram, and how many per ml., if the density = 1.05?

Determination of sodium bicarbonate and sodium carbonate in a mixture.

Method 1. This method is especially recommended for those cases in which the sample contains small amounts of bicarbonate and relatively large amounts of carbonate. The total alkalinity of the sample is first determined by titration with standard acid, with methyl orange, methyl yellow, bromphenol blue, or bromcresol green as indicator (see the standardization of acid with sodium carbonate):

$$Na_2CO_3 + 2\,HCl \rightarrow 2\,NaCl + H_2O + CO_2$$
$$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2.$$

The bicarbonate content is then determined by adding standard base to a solution of the sample in excess of the amount which is required to transform the bicarbonate into carbonate. All the carbonate is removed from the solution by adding an excess of barium chloride, and the excess alkali is finally titrated back without filtering, phenolphthalein being used as indicator.

$$NaHCO_3 + NaOH \rightarrow Na_2CO_3 + H_2O$$
$$Na_2CO_3 + BaCl_2 \rightarrow BaCO_3 + 2\ NaCl.$$

Since barium carbonate is the salt of a strong base and a very weak acid, it is strongly hydrolyzed in solution. Its solubility, however, is very small and is, moreover, diminished by the excess of barium salt present. A suspension of barium carbonate in a solution containing barium chloride is neutral towards phenolphthalein, since the carbonate-ion concentration, and therefore the concentration of the hydroxyl ions formed by hydrolysis, is negligibly small. The color change from red to colorless in the white suspension can be observed very sharply.

From the amounts of acid used in the determination of the total alkalinity and the amount of sodium hydroxide required to transform the bicarbonate into carbonate, it is possible to calculate the carbonate and bicarbonate content of the sample.

Procedure. Weigh out 1.5 to 2 g. of sample and transfer to a 250 ml. volumetric flask. Make the solution up to the mark with equilibrium water and mix thoroughly.

Total alkalinity. Titrate 25.00 ml. of the solution with 0.1 *N* standard acid, using methyl yellow or any other indicator changing color near a pH of 4. The end point is reached when the indicator assumes an orange-red color. A sharper color change is obtained with the mixed indicator methyl orange-indigo carmine (p. 450); the end point is then reached when the indicator changes from neutral gray to violet. For a more exact determination of the end point see "standardization of acid," page 548.

Sodium bicarbonate content. Add 25.00 ml. of 0.1 *N* sodium hydroxide solution to 25 ml. of the sample and immediately thereafter 10 ml. of 10 per cent barium chloride solution and 2 drops of phenolphthalein (or thymol blue). Back-titrate the suspension immediately with standard 0.1 *N* hydrochloric acid. The end point is reached when the color changes from pink to colorless (or from bluish to yellow if thymol blue is used). Run a blank under exactly the same conditions with 25.00 ml. of standard base, 25 ml. of water, and 10 ml. of barium chloride solution. The difference between the amounts of acid used in the blank and in the determination itself corresponds to the sodium bicarbonate content of the solution.

NOTES:

1. The method described is also very useful in the determination of the carbonate content of commercial alkali hydroxides. In this case the sum of carbonate and hydroxide is determined by titration with acid (methyl yellow as indicator), and then the hydroxide alone after removing the carbonate by precipitation with barium chloride. The method is also used for testing C. P. sodium carbonate for the presence of sodium hydroxide or sodium bicarbonate (p. 547).

2. The method is often applied to the determination of bicarbonate and carbonate in boiler water. In these cases too much bicarbonate will be found, since sulfate, which is always present in boiler water, interferes. If barium sulfate is precipitated from a solution containing an excess of hydroxyl ions, part of the latter are coprecipitated and, consequently, high results are obtained. If the sulfate content of the sample is known, a blank can be run with the same amount of sulfate, following the same procedure that is used in the determination.

3. Carbon dioxide in the free state, or bound as bicarbonate or carbonate, can be determined by evolution from an acid medium and absorption in an excess of standard barium hydroxide, or of standard sodium hydroxide containing an excess of barium chloride. It should be stated that the absorption of the carbon dioxide by the alkaline solution is relatively slow, and part of the gas may escape if it is bubbled through only one bottle containing the standard base. Therefore it is necessary to pass the gas through a number of bottles in succession with known volumes of standard base or, better, to work in a closed system and circulate the gas a few times through the one bottle containing the standard base and barium salt.

4. The alkaline earth metals yield slightly soluble carbonates. Therefore they can be determined by treating their neutral solutions with an excess of standard sodium carbonate and then titrating the excess in an aliquot part of the filtrate with standard acid, methyl yellow being used as indicator. It is also possible to make the determination by precipitating calcium, strontium, or barium with an excess of a sodium carbonate solution, filtering and washing the precipitate with 50 per cent alcohol, and finally dissolving it in an excess of standard acid. The excess acid is back-titrated with standard base.

Method 2. In the discussion of the neutralization curve of carbonic acid (see Table LXII, p. 462, and Fig. 82, p. 461) it was shown that a solution of sodium bicarbonate has a pH of 8.35 and that near this point the pH changes relatively slowly upon addition of a slight excess of sodium carbonate or carbon dioxide. Therefore if sodium carbonate is titrated to bicarbonate with standard acid:

$$Na_2CO_3 + HCl \rightarrow NaHCO_3 + H_2O,$$

there is no indicator which will give a sharp color change.

In order to obtain good results, the titration must be continued until the pH has reached a value of 8.35, which is the pH at the theoretical end point. This can be done by employing phenolphthalein or thymol blue as indicator and using for comparison a solution of sodium bicarbonate which has the same volume and concentration as the unknown at the end point and which contains the same amount of indicator. The end point is reached when the solution titrated has the same color as the comparison solution. It is still simpler to use a mixed indicator. Simpson [1] has recommended the use of a mixture of 6 parts thymol blue and 1 part cresol red as a mixed indicator. The mixture has a purple color in the carbonate solution; in the neighborhood of the equivalence point it changes to blue. In making the titration, the acid is added slowly, until the solution assumes a rose color. This is the end point; upon further addition of acid the color changes to orange-yellow. The end point can be found with an accuracy of 0.5 per cent without a comparison solution. This method is not as accurate as the first one, if the sample contains a large excess of sodium bicarbonate.

Procedure. Use the same solutions as in Method 1, and determine the total alkalinity (the sum of carbonate and bicarbonate) in the same way as there described.

Sodium carbonate content. Add a few drops of the mixed indicator (see above) to 25.00 ml. of the solution, and titrate with 0.1 *N* standard acid until the color changes from blue to pink.

NOTES:

1. Free carbon dioxide which occurs in most natural waters and also in distilled water can be titrated as a monobasic acid:

$$H_2CO_3 + NaOH \rightarrow NaHCO_3 + H_2O$$

by using the mixed indicator, phenolphthalein, or thymol blue for the detection of the end point. In such titrations it is always noticed that the color of the indicator becomes alkaline before the end point is reached. The reason is that most of the carbon dioxide is present in the free state, and a small part only (less than 1 per cent) as carbonic acid:

$$CO_2 + H_2O \rightleftarrows H_2CO_3.$$

The carbonic acid reacts instantaneously with the base. The equilibrium is then disturbed, and the carbon dioxide, not being an acid, must first form carbonic acid before reacting with alkali. Therefore if a carbon dioxide solution is titrated with standard base, with phenolphthalein as an indicator, the color will turn pink very early in the titration, although the greater part of the carbon dioxide is still in the solution in the free state. After one-half to one minute, the liquid will turn colorless. This phenomenon will be repeated until all of the carbon dioxide has been transformed into bicarbonate. The end point is reached when the basic color of the indicator persists for at least five minutes.

---

[1] S. G. Simpson, Ind. Eng. Chem. *16*, 709 (1924).

More or less carbon dioxide will escape from the solution during such a titration. Therefore it is necessary first to make a preliminary titration to the permanent end point. A second titration is then made, and nearly the required amount of alkali as found in the first titration is added all at once, and from then on the addition is continued carefully to the end point.

2. Carbon dioxide can be determined in the above way in the presence of bicarbonate, and the latter can be determined with standard acid with methyl yellow as an indicator. It is also possible to determine the sum of carbon dioxide and bicarbonate by adding an excess of standard base and barium chloride, or of standard barium hydroxide, and then titrating back with standard acid, using phenolphthalein as indicator (Method 1).

$$CO_2 + 2\ NaOH \rightarrow Na_2CO_3 + H_2O$$
$$NaHCO_3 + NaOH \rightarrow Na_2CO_3 + H_2O$$
$$Na_2CO_3 + BaCl_2 \rightarrow BaCO_3 + 2\ NaCl.$$

Boric acid and borax.

Boric acid is such a weak acid that it cannot be titrated accurately with 0.1 *N* standard alkali. (The ionization constant of boric acid is 5×10^{-10}; cf. the discussion on p. 456, and Fig. 81.) However it can be transformed into a relatively strong acid by adding organic hydroxyl compounds containing more than one hydroxyl group per molecule, such as glycerol, mannitol, dextrose, or invert sugar. These polyvalent alcohols form complex acids with boric acid which are much stronger than the boric acid alone. Mannitol is more effective than glycerol; 0.5 to 0.7 g. of the former per 10 ml. of solution is sufficient. It is much more economical, however, to use a solution of invert sugar for the purpose. This is prepared in the following way: About 3 kg. of sucrose are dissolved in 1 liter of distilled water, and the liquid is boiled several minutes until clear, best in a large tinned vessel. Then 25 ml. of 3 *N* sulfuric acid are added quickly; and, after stirring for one-half minute, the solution is treated with 1½ liters of water to which 25 ml. of 3 *N* carbonate-free sodium hydroxide have been added, stirred again, and cooled. The resulting solution should be neutral and colorless; it contains about 55 per cent of invert sugar.

For every 10 ml. of 0.1 *N* boric acid, 3 to 4 ml. of invert sugar solution are added, and the solution is then titrated to a faint pink with phenolphthalein as indicator. Then 5 ml. more of the invert sugar solution are added. If the color of the indicator vanishes, more alkali is added until the pink color appears, and then more invert sugar is added. This procedure is repeated until the addition of invert sugar no longer causes a fading of the pink color. The invert sugar solution should be very carefully neutralized to phenolphthalein just before its use.

Sodium tetraborate ($Na_2B_4O_7 \cdot 10\ H_2O$ = borax). Borax in solution can be considered as boric acid which is 50 per cent neutralized:

$$Na_2B_4O_7 + 5\ H_2O \rightleftarrows 2\ NaH_2BO_3 + 2\ H_3BO_3.$$

The NaH_2BO_3 can be titrated with standard acid (methyl red, bromcresol green, methyl yellow, methyl orange, or bromphenol blue as indicator):

$$NaH_2BO_3 + HCl \rightarrow H_3BO_3 + NaCl$$

or

$$Na_2B_4O_7 + 2\ HCl + 5\ H_2O \rightarrow 4\ H_3BO_3 + 2\ NaCl.$$

Therefore this titration gives the amount of alkali bound to the boric acid.

Another portion of the sample can be titrated with standard base in the presence of invert sugar:

$$[H_3BO_3\text{ complex}] + NaOH \rightarrow [NaH_2BO_3\text{ complex}] + H_2O$$
$$Na_2B_4O_7 + 2\ NaOH + 3\ H_2O \rightarrow 4[NaH_2BO_3\text{ complex}].$$

If the borax is pure, the amount of standard acid required in the titration with methyl red as indicator is equal to the amount of standard base used in the titration with phenolphthalein in the presence of invert sugar. In the following procedure commercial borax, which usually is partly dehydrated, may be used as the sample.

Procedure. Weigh out 3 to 5 g. of sample, transfer to a 250 ml. volumetric flask, and make up to the mark.

Titration of the alkali. Pipet 25 ml. of the well-mixed solution into a flask, add 3 drops of methyl red, and titrate with 0.1 *N* standard acid until the color changes to orange-red.

Titration of the boric acid. Pipet 25 ml. of the solution into a flask; add 10 ml. of the neutral invert sugar solution and 3 drops of phenolphthalein. Titrate with 0.1 *N* standard alkali to the color change of the indicator. Add 5 ml. more of the invert sugar solution, and continue the titration if the liquid becomes colorless. Repeat the test by adding more invert sugar.

Calculation. Calculate the number of equivalents of alkali and boric acid in the sample. If the salt has the composition $Na_2B_4O_7 \cdot x\ H_2O$, the number of equivalents of alkali required is equal to that of boric acid.

Calculate the $Na_2B_4O_7$ and water content of the sample in per cent.

Phosphoric acid, H_3PO_4.

$$H_3PO_4 \rightleftarrows H_2PO_4^- \qquad K_1 = 7 \times 10^{-3};\ pK_1 = 2.16$$
$$H_2PO_4^- \rightleftarrows H^+ + HPO_4^= \qquad K_2 = 7 \times 10^{-8};\ pK_2 = 7.16$$
$$HPO_4^= \rightleftarrows H^+ + PO_4^{\equiv} \qquad K_3 = 5 \times 10^{-13};\ pK_3 = 12.3.$$

Phosphoric acid as a monobasic acid.

$$H_3PO_4 + NaOH \rightarrow NaH_2PO_4 + H_2O.$$

The pH of a solution of monosodium phosphate is found from the equation (see p. 460) to be

$$pH = \tfrac{1}{2}(pK_1 + pK_2) = 4.66.$$

Experimentally it is found that a 0.05 to 0.01 *M* solution of monopotassium phosphate has a pH of 4.4 to 4.45. The change of the pH near the equivalence point is not very pronounced. If methyl orange or bromcresol green is used as indicator, it is desirable to employ a solution of monopotassium phosphate with the same amount of indicator for comparison. Calcium and magnesium do not affect the determination of the end point.

Phosphoric acid as a dibasic acid. The pH of a 0.05 *M* disodium phosphate solution is 9.6. At this pH, phenolphthalein and thymol blue exist in their alkaline forms. Therefore if phosphoric acid is titrated as a dibasic acid with phenolphthalein or thymol blue as indicator, the color change will occur too early. However, if at the point at which the indicator shows a color change to the alkaline side, the solution be half-saturated with sodium chloride, the hydrolysis is repressed and the final color change occurs at the theoretical end point.

Thymolphthalein begins to change color at a pH of 9.7 and therefore will just show a color change to bluish at the end point. In this case no sodium chloride should be added, and the standard base used must be carbonate-free.

It is possible first to titrate phosphoric acid as a monobasic acid with methyl orange or methyl yellow as indicator. After the first end point is reached, a few drops of thymolphthalein can be added and the titration continued to the second end point.

NOTE:

Calcium and magnesium interfere in the titration of phosphoric acid as a dibasic acid, since in the presence of these metals precipitates of indefinite composition are formed. The interference can be prevented by the addition of an excess of neutral 10 per cent potassium oxalate after the first end point (methyl orange) has been reached. The precipitate of calcium oxalate does not render the color change of thymolphthalein or phenolphthalein less sharp. Barium, if present, can be made harmless by the addition of sulfate after the first end point has been reached.

Phosphoric acid as a tribasic acid.[1] The third dissociation constant of phosphoric acid is so small that the third hydrogen cannot be titrated. If the trivalent phosphate ion is precipitated, titration as a tribasic acid is possible. Precipitation with calcium chloride is especially adapted to the purpose. One must work under the proper conditions, for otherwise a secondary phosphate or a strongly basic calcium phosphate may precipitate.

Ammonia in an ammonium salt.

Ammonia is a weak base which is volatile. Therefore if an excess of a strong base is added to a solution of an ammonium salt and the mixture is distilled, the ammonia will be quantitatively expelled. Since ammonia volatilizes from its aqueous solutions at room temperature, it is necessary to absorb it in an excess of standard acid. The excess of acid can be back-titrated in the presence of methyl red (or methyl orange, bromcresol green, methyl yellow, or bromphenol blue) as indicator. (Why not phenolphthalein?)

---

[1] For procedure see I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis* Vol. II.

A convenient form of distillation apparatus for this determination is shown in Figure 114. It consists of a 500 ml. long-necked Pyrex flask (Kjeldahl flask), to the top of which a spray trap is attached by means of a rubber stopper as shown. The purpose of the trap is to prevent droplets of the strongly alkaline liquid from being carried over into the condenser. The lower limb of the trap, which projects down into the neck of the flask, should have a beveled end to facilitate the return flow of liquid condensed in the trap. The upper limb of the trap is connected to an ordinary glass condenser by means of a rubber stopper; the delivery tube should extend well into the cooled part of the inner tube of the condenser. The lower end of the condenser is provided with an adapter tube attached by means of a rubber stopper. The end of the adapter dips into the standard acid contained in the 250 ml. Erlenmeyer flask which serves as a receiver.

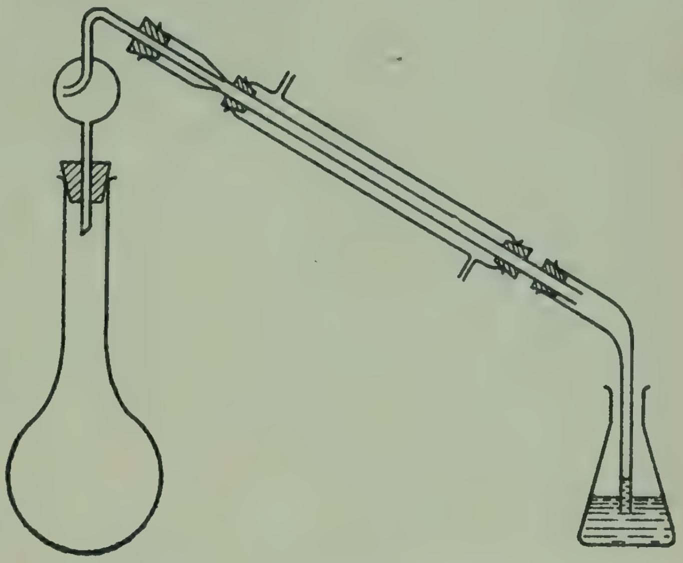


FIG. 114. Apparatus for ammonia distillation.

Procedure. Weigh out a 1.5 to 2.0 g. sample of crude ammonium sulfate into a 250 ml. volumetric flask; dissolve the salt in water, dilute to the mark, and mix thoroughly. Pipet 25 ml. of the solution into the distillation flask and dilute with 100 ml. of water.

Pipet 50 ml. of 0.1 N standard hydrochloric acid into the receiver, and adjust the flask so that the end of the adapter tube barely dips beneath the surface of the acid.

Add about 1 g. of granulated zinc to the solution in the distillation flask.[1] When all is in readiness, with the spray trap connected to the condenser and the receiver in place, quickly pour 50 ml. of cold 50 per cent sodium hydroxide solution into the flask, and connect the latter immediately to the trap and condenser. Gently shake the contents of the flask with a rotary motion, and place a burner under the flask at once. It is very important to perform these operations as quickly as possible to prevent loss of ammonia.

---

[1] The purpose of the zinc is to prevent "bumping" during the subsequent distillation of the strongly alkaline liquid. The zinc reacts slowly with the sodium hydroxide solution with the evolution of hydrogen, which comes off in a fine stream of bubbles from each zinc particle. The fine gas bubbles prevent superheating of the liquid, which is the cause of "bumping." If nitrate is present, zinc cannot be used, because nitrate is reduced to ammonia by zinc in alkaline solution (see note 2 below); in such a case small pieces of porous porcelain plate should be employed.

Heat the contents of the flask rapidly to boiling, and then adjust the flame so that the boiling is continuous but not too rapid. The receiver should be carefully attended to during the distillation, because there is a tendency for some of the receiving acid to be drawn up into the condenser. This danger is minimized by bringing the liquid in the flask to boiling as quickly as possible and by adjusting the receiver so that the end of the adapter dips only slightly into the solution. When the distillation is correctly performed, there should be a gentle oscillation of a short column of the acid in the lower end of the adapter, but there should be no escape of bubbles from its end after the air has been expelled.

Continue the distillation until about two thirds of the liquid in the flask has distilled over. Then lower the receiver so that the end of the adapter is out of the acid, and remove the flame from the flask. Do not remove the flame until the receiver has been lowered, otherwise part of the acid may be sucked back. Disconnect the adapter from the condenser, and rinse it out into the flask with a small amount of water from the wash bottle. Add a few drops of methyl red indicator, and titrate the excess acid in the solution with 0.1 *N* sodium hydroxide (color change from red to yellow). Calculate the percentage of nitrogen and also of ammonia in the sample. In the most accurate work run a blank.

NOTES:

1. Instead of absorbing the ammonia in an excess of standard acid, it is possible to reduce the volatility of the ammonia in water by adding a very weak acid. For this purpose there may be used 50 ml. of a solution of 4 per cent boric acid in equilibrium water. The boric acid solution should be kept cool during the distillation. In the titration of the ammonia, 50 ml. of a solution of the boric acid, mixed with enough water to make the volume equal to that of the solution at the end point and containing the same amount of indicator (methyl red or, better, bromcresol green), is used for comparison. The titration is continued slowly until the colors of the two liquids are identical.

2. Nitrate can be reduced quantitatively to ammonia with the aid of certain alloys. Arnd's alloy,[1] consisting of 60 per cent copper and 40 per cent magnesium, is very useful.

About 0.25 g. of the nitrate dissolved in 200 ml. of water is transferred to the distillation flask, 10 ml. of a 20 per cent magnesium chloride ($MgCl_2 \cdot 6\ H_2O$) solution and 5 g. of the finely pulverized alloy are added, and the whole is boiled until about two thirds of the liquid has distilled over. The distillate is received in 50 ml. of 0.1 *N* standard acid or in a boric acid solution.

---

[1] Th. Arnd, Z. angew. Chem. *30*, 169 (1917); *33*, 296 (1920).

Determination of crude protein in flour or wheat (Kjeldahl[1] nitrogen determination).

The proteins comprise a group of complex nitrogen-containing compounds which constitute one of the three classes of important nutrient materials present in foods (carbohydrates, fats, and proteins). When protein-containing material is heated with concentrated sulfuric acid in the presence of mercury[2] as a catalyst to speed up the reaction, the acid is gradually reduced to sulfur dioxide and water, while the carbon and hydrogen of the organic material are oxidized to carbon dioxide and water, and the nitrogen is transformed into ammonium sulfate. The latter is determined by adding an excess of alkali to the solution after the digestion with acid, and distilling in the manner described under the ammonium determination (p. 563). The percentage of protein is found by multiplying the percentage of nitrogen by a factor which varies with the nature of the protein present in the sample. For the protein in wheat and flour the factor commonly used is 5.7. The results obtained are referred to as *crude protein.*

Procedure. Weigh out a 1.5 to 2.0 g. sample of flour or ground wheat,[3] and transfer to a *dry* 800 ml. Kjeldahl flask of Pyrex glass. Weigh out roughly 10 g. of anhydrous sodium sulfate (or potassium sulfate) and 0.6 to 0.8 g. of mercuric oxide, and add the mixture to the flask. Pour 25 ml. of concentrated sulfuric acid into the flask in such a way that any solid adhering to the neck is washed down.

Support the flask in an inclined position on a ring stand (or on the special rack provided for this purpose) in a well-ventilated hood, and heat the contents gently with a small flame. The mixture will froth and turn black at first. When the frothing ceases to be vigorous, increase the flame until the mixture boils gently. As the digestion proceeds, the original black color gradually fades to brown, and finally the solution becomes perfectly colorless. Continue the heating for fifteen minutes after the solution has become colorless; then remove the flame and allow the flask to cool. The liquid will solidify to a mass of crystals or a solid cake on cooling.

When the flask has cooled to at least 50°, carefully add 200 ml. of water, and swirl the flask until the solid material has dissolved completely. Cool the solution to room temperature under the tap, and add 10 ml. of 5 per cent potassium sulfide solution to precipitate the mercury. Then add granulated zinc and sodium hydroxide, and distill off the ammonia in exactly the same manner as described under the determination of ammonia (p. 563).

Calculate the percentage of nitrogen in the sample, and multiply the value obtained by 5.7 to obtain the percentage of "crude protein."

In the most accurate work run a blank on the reagents through all the steps of the procedure, and correct the result obtained in the analysis of the sample.

---

[1] J. Kjeldahl, Z. anal. Chem. *22*, 366 (1883).

[2] Copper sulfate and selenium can also be used as catalysts in the digestion. Alkali sulfates are often added also to raise the boiling point of the mixture and hasten the reaction.

[3] Samples should be kept in well-closed bottles, as the water content changes markedly with varying humidity of the atmosphere.

PROBLEMS

1. 0.4212 g. of pure potassium tetraoxalate, $KHC_2O_4 \cdot H_2C_2O_4 \cdot 2\,H_2O$, require 48.90 ml. of sodium hydroxide solution for neutralization with phenolphthalein as indicator. Calculate the normality of the sodium hydroxide. *Ans.* 0.1017 *N*.

2. A precipitate of calcium oxalate obtained from a 0.5004 g. sample of limestone is ignited to give a mixture of calcium carbonate and oxide which is then dissolved in 50.00 ml. of 0.2000 *N* hydrochloric acid. 4.50 ml. of 0.1060 *N* sodium hydroxide are required for the back-titration of the excess acid (bromcresol green as indicator). What is the percentage of calcium carbonate in the limestone? *Ans.* 95.24 per cent.

3. 100 ml. of a natural water require 41.0 ml. of 0.0200 *N* acid for neutralization against methyl orange, and 2.0 ml. of the same acid against phenolphthalein. Calculate the HCO_3^- and $CO_3^=$ content of the water in mg. per liter. *Ans.* 452 mg. HCO_3^- and 24 mg. $CO_3^=$ per l.

4. It is found that 4.1 ml. of 0.0100 *N* sodium hydroxide are needed for the titration of 200 ml. of distilled water when the indicator used is phenolphthalein. What is the CO_2 content of the water in mg. per liter? *Ans.* 9.02 mg. CO_2 per l.

5. How can sulfuric and boric acids be determined with standard base in a mixture of the two in water?

6. The sum of calcium and magnesium in a boiler water is determined after neutralizing the sample to methyl orange by precipitation of the calcium and magnesium with a standard mixture of sodium hydroxide and sodium carbonate, the excess being titrated in an aliquot part of the filtrate with standard acid. What is the composition of the precipitate? What indicator should be used in the back-titration with standard acid? 50.00 ml. of the standard alkali mixture required 70.54 ml. 0.0910 *N* acid. In the actual determination 100 ml. of the alkaline mixture were added to 100 ml. of the solution and the mixture diluted to 250 ml. 100 ml. of the filtrate required 12.00 ml. of 0.0910 *N* acid. What is the sum of the number of equivalents of calcium and magnesium in 1 liter of the water? *Ans.* 0.1011 equivalent per l.

7. An unweighed sample of calcium phosphate is dissolved in 50.00 ml. of 0.0500 *N* hydrochloric acid. 10.12 ml. of 0.0490 *N* base are required to back-titrate the excess acid, methyl orange being used as indicator. The pH at the end point is 4.5. After reaching the first end point, an excess of neutral potassium oxalate is added and the titration continued to the color change of thymolphthalein. If 30.15 ml. of 0.0490 *N* alkali are used between the first and second end point, what is the ratio of CaO to P_2O_5 in the sample of calcium phosphate? *Ans.* 1 CaO : 0.423 P_2O_5.

8. A commercial product of sodium phosphate was found to consist of a mixture of Na_3PO_4, Na_2HPO_4, and water of crystallization. How can the composition of the sample be determined by titration with acid using two different indicators?

9. Devise a method for determining sodium carbonate and borax in a mixture consisting only of these two substances and water, by simple acidimetric and alkalimetric titrations.

10. A solution of hydrochloric acid is standardized by adding an excess of ammonia to 100.00 ml., evaporating to dryness, and weighing the residue,

which was found to have a weight of 0.5350 g. Calculate the normality of the acid.

11. A solution of pure lead nitrate is saturated with hydrogen sulfide. The precipitate is filtered off and washed, and the filtrate is titrated with sodium hydroxide, methyl orange being used as an indicator; 24.50 ml. of 0.5000 *N* sodium hydroxide are required. Calculate the amount of lead in the sample solution.

CHAPTER XXXV

ARGENTIMETRIC AND MERCURIMETRIC DETERMINATIONS

Preparation of standard solutions.

Silver nitrate. Metallic silver can be obtained in a very pure state.[1] However, it is not very suitable for the preparation of standard silver solutions, because it must be dissolved in nitric acid, and the excess of acid must then be removed in most cases. Therefore it is preferable to prepare standard silver solutions by dissolving exactly weighed amounts of pure silver nitrate in water.

Very pure preparations of silver nitrate can be purchased. Impure products can be purified by recrystallization from dilute nitric acid. The crystals are collected in a glass filter crucible or a Büchner funnel with a sintered-glass disk in order to prevent contamination by shreds of filter paper or traces of organic substances which exert a reducing action on the salt. The salt is dried at 110° and then, protected from dust, is heated fifteen minutes at 220° to 250° (melting point is 208°). Fusion of the salt is required to remove the occluded water in the crystals, which is not expelled by heating at 110°. Large unmelted crystals which are otherwise pure may contain 0.1 to 0.2 per cent of water. The heating should not be continued for too long a period, nor at a temperature higher than 250° because silver nitrate will then slowly decompose with the formation of silver nitrite. The dried salt can be kept unchanged in a glass-stoppered bottle; it is not hygroscopic.

Prepare 500 ml. of 0.1000 N silver nitrate solution by weighing out the proper amount of pure dried silver nitrate,[2] dissolving in water, and diluting to volume. Protect the solution from the light.

Sodium chloride. Although it is not necessary to standardize the silver nitrate solution, if it has been prepared from a pure product, it is desirable to have available a standard chloride solution to check the titer of the silver solution after the lapse of time.

Pure sodium chloride is prepared by precipitation of a filtered saturated solution of a C. P. product with concentrated hydrochloric acid or hydrogen chloride (p. 168). The precipitated salt is filtered off with suction, washed with water, dried, ground to a powder, and heated in an electric furnace at 500°–600° to constant weight. One may heat over a gas flame if the crucible is placed in a hole in an inclined asbestos board to prevent the entrance of sulfur-containing gases from the burner that might contaminate the salt.[1]

---

[1] T. W. Richards and R. G. Wells, J. Am. Chem. Soc. 27, 459 (1905).

[2] For student purposes it is sufficient to use a pulverized analytical reagent dried at 150°

Prepare 500 ml. of 0.1000 *N* sodium chloride solution by weighing out the calculated amount of the pure salt, dissolving in water, and diluting to volume.

Potassium thiocyanate. Potassium thiocyanate of reagent quality has been found to be 99.9 per cent pure.[2]

It can be further purified by two recrystallizations from water. The product is first dried in a desiccator at room temperature and then in an oven at 120°–150°. When thus dried, the salt contains only a few hundredths of a per cent of occluded water. The last small trace of water can be removed by fusing the salt for two to three minutes at 190°–200°. The pure dry salt is not appreciably hygroscopic in an atmosphere of less than 45 per cent relative humidity. It should be kept protected from light and acid fumes.

Prepare 500 ml. of 0.1000 *N* solution by weighing out 4.856 g. of the pure dry salt, dissolving in water, and diluting to volume. Solutions of pure potassium thiocyanate in pure water are quite stable.

EXERCISES

Checking the titer of the standard sodium chloride solution against the standard silver nitrate solution. The Mohr titration.

The theory of the Mohr titration has been discussed on page 471.

Indicator solution: A 5 per cent solution of potassium chromate in water. One ml. of indicator is used for volume of 50 to 100 ml.

Procedure. Pipet 25 ml. of 0.1000 *N* sodium chloride solution into a 250 ml. Erlenmeyer flask, add 1 ml. of indicator solution, and slowly titrate with 0.1 *N* silver nitrate solution, swirling the liquid constantly, until the first permanent color deviation from the pure yellow of the suspension is obtained.

Determine the indicator blank by adding 1 ml. of the indicator to 50 ml. of water or, better, to 50 ml. of a suspension of a little chloride-free calcium carbonate (a few hundred mg.), and then silver nitrate until the color of the blank matches that of the solution titrated. The indicator blank, which should not amount to more than 0.03–0.05 ml. of 0.1 *N* silver nitrate, is deducted from the volume of silver nitrate used in the titration.

Calculate the normality of the silver nitrate solution.

---

[1] For purity tests compare I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis*, Vol. II.

[2] I. M. Kolthoff and J. J. Lingane, J. Am. Chem. Soc. *57*, 2126 (1935).

Determination of chloride in a soluble chloride according to Mohr.

Weigh out 2–2.5 g. of an alkali chloride sample, dissolve in water, and dilute to 250 ml. in a volumetric flask. Pipet out 25 or 50 ml. (requiring between 25 and 40 ml. silver nitrate), and titrate according to the procedure described above. Report the percentage of chlorine. The remainder of the solution is to be reserved for the titration with an adsorption indicator, and according to Volhard.

NOTES:

1. Bromides can be titrated in the same way as chlorides. The Mohr method does not give satisfactory results in the titration of iodides and thiocyanates because of adsorption phenomena.

2. The titration must be carried out in neutral or weakly alkaline solution (p. 473); the pH should lie between 6.5 and 10.5 at room temperature. Acid solutions are conveniently neutralized with chloride-free borax, sodium bicarbonate, or calcium carbonate.

3. Pure ammonium chloride can be titrated according to the standard procedure. If the solution is acid, the pH should be adjusted to a value between 6.5 and 7.2. At a higher pH too much free ammonia is formed, which increases the solubility of silver chloride and silver chromate; and the color change then appears too late.

4. Chlorides of cations which are hydrolyzed and give solutions of distinctly acid reaction (aluminum, iron, bismuth, tin, zinc, etc.) cannot be titrated according to the method of Mohr. Basic salts containing chloride precipitate upon the adjustment of the pH. Neither can the method be applied to the titration of solutions containing copper, nickel, and cobalt salts, the cations of which are colored. Lead and barium yield slightly soluble chromates with the indicator and interfere in the titration; barium can be made harmless by the addition of an excess of sodium sulfate.

5. The titration cannot be made in the presence of anions yielding slightly soluble silver salts, such as phosphate, arsenate, pyrophosphate, sulfite, sulfide, carbonate, oxalate, etc. Sulfite can be made harmless by oxidation to sulfate, and hydrogen sulfide can be removed by boiling. Anions which do not form slightly soluble or complex silver salts do not interfere and may be present in large quantities. If, however, the solution contains large amounts of noninterfering ions, the silver chromate formed by a local excess of reagent exhibits a marked tendency to agglomerate. It then reacts slowly with the chloride ions which are still present, so that the end point may apparently be reached too early. Under these conditions it is necessary to shake vigorously near the end point and to add silver nitrate until the reddish-brown color no longer disappears after shaking and allowing the solution to stand.

6. The reverse titration of silver with chloride using chromate as indicator does not give good results, because the flocculated silver chromate reacts too slowly with chloride.

Chloride titration with an adsorption indicator.

Before making this titration the student should read pages 115, 473.

Indicator: (a) 0.1 per cent fluorescein in 70 per cent alcohol or 0.1 per cent sodium fluoresceinate in water, or

(b) 0.1 per cent dichlorofluorescein in 70 per cent alcohol, or 0.1 per cent sodium dichlorofluoresceinate in water.

Procedure. Pipet 25 or 50 ml. of the chloride solution (see p. 570) into a 250 ml. Erlenmeyer flask. Add 5 to 10 drops of either indicator, and titrate the solution with silver nitrate in diffuse light with constant swirling. The silver chloride sol flocculates approximately 1 per cent before the equivalence point. Continue the titration dropwise with vigorous agitation until the precipitate suddenly becomes reddish. The indicator blank cannot be determined directly owing to the great sensitiveness of the precipitate toward light; the correction fortunately is negligibly small with 0.1 *N* silver nitrate.

NOTES:

1. The determination gives exact results in the titration of chlorides, bromides, iodides, and thiocyanates.
2. The method cannot be applied to the titration of solutions more dilute than 0.005 *N*.
3. The pH should be the same as that in the Mohr titration when fluorescein is used as indicator. Dichlorofluorescein, being a stronger acid than fluorescein, gives good results when the pH is greater than 4. For this reason the chlorides of copper, nickel, manganese, zinc, and aluminum, which cannot be titrated according to Mohr, can be determined by a direct titration when dichlorofluorescein is used as indicator.
4. The interference of anions is the same as in the Mohr titration. Large amounts of electrolytes which do not yield insoluble silver salts may obscure the end point. The coagulation of the silver halide then begins early in the titration, and the end point becomes less distinct.

Determination of bromide in alkali bromide with eosin as indicator.

(For theory see p. 473.)

Indicator: Eosin, 0.1 per cent solution in 70 per cent alcohol, or 0.1 per cent solution of the sodium salt in water.

Procedure. Add 10 drops of indicator and a few ml. of 6 *N* acetic acid to 50 to 100 ml. of the neutral bromide solution, which should not be more concentrated than 0.05 *N*. Titrate with silver nitrate, with constant agitation, in diffuse light. Approximately 1 per cent before the equivalence point the silver bromide flocculates. Continue the titration dropwise with vigorous stirring or shaking until the precipitate suddenly becomes colored intensely red. The indicator blank is negligibly small.

NOTES:

1. Iodide and thiocyanate can be determined in the same way. With chloride the color change occurs much too early (for interpretation see p. 474)
2. The titration yields good results at pH values between 3 and 10.
3. Even in the titration of very dilute solutions (0.001 *N*) a sharp color change is obtained.

Titration of iodide in an alkali iodide to the "clear point."

(For theory see p. 470.) Dilute the solution of the iodide to a concentration of less than 0.04 *N*. Carefully titrate with silver nitrate with constant shaking. Approximately 1 per cent before the equivalence point, the silver iodide begins to flocculate. Continue the titration carefully, with vigorous shaking after each addition of reagent, until the supernatant liquid is perfectly clear. The end point can be determined with great precision in solutions of pure iodide.

Titration of iodide in the presence of chloride with di-iodofluorescein as adsorption indicator.

Indicator: 0.5 per cent di-iodofluorescein in 70 per cent alcohol (dimethyl di-iodofluorescein and Bengal red are also suitable indicators).

Procedure. Add 1 to 2 ml. of the indicator to 50 to 100 ml. of the solution, which should not be stronger than 0.02 *N* in iodide. Titrate with 0.1 *N* silver nitrate until the color changes from orange-red to a bluish-red. The color change is not very sharp; it goes through a brownish-red and then a carmine-red before the end point. For exact determinations it is indispensable to use at the end point a reference solution of the same composition as the system titrated. The color change in the presence of chloride comes a little late; 0.8 per cent of the amount of silver nitrate required should be subtracted as a correction.

NOTE:

Iodide ions are much more strongly adsorbed on silver iodide than are chloride ions; the indicator ions are adsorbed to a less extent than the iodide and much more strongly than the chloride ions. Therefore after all the iodide has been transformed into silver iodide, the indicator will be adsorbed, and the color change then occurs. The precipitation of iodide is quantitative before the chloride begins to precipitate.

Titration of silver according to the Volhard method. (See p. 475.)

Indicator: Saturated solution of ferric ammonium sulfate in water (approximately 40 per cent).

Procedure. Add 1 ml. of indicator solution to 25 to 40 ml. of standard silver nitrate solution, acidify with 5 ml. of 6 *N* nitric acid, and titrate with thiocyanate. The first perceptible color change to *orange-red* occurs about 1 per cent before the equivalence point, owing to the fact that silver ions are present on the surface of the precipitate in the adsorbed state. After the first color change has occurred, continue the titration carefully with vigorous agitation to the appearance of a brownish tinge which is permanent on strong shaking. The indicator blank amounts to 0.01 ml. of 0.1 *N* silver nitrate. Calculate the normality of the thiocyanate solution.

Determination of chloride in a suitable sample according to Volhard's method.

(For the theory see p. 475.)

Procedure 1. Add 5 ml. of 6 *N* nitric acid to 25 to 50 ml. of the chloride solution (see p. 570), and then add a measured excess of standard silver nitrate solution. Filter, and wash the precipitate thoroughly with dilute nitric acid. Add to the combined filtrate and washings 1 to 2 ml. of ferric alum solution, and titrate the excess silver as described in the preceding exercise. Write the equations for the reactions involved, and calculate the chloride content of the solution.

NOTE:

Instead of filtering off and washing the silver chloride, the following procedure may be applied: Add nitric acid and an excess of silver nitrate to a measured volume of the chloride solution in a volumetric flask of 100 or 250 ml. capacity. Make up to the mark, mix thoroughly, and filter into a dry flask, discarding the first 5 or 10 ml. of the filtrate. Pipet an aliquot part, e.g., 50 ml., of the filtrate into a clean flask, and titrate the excess of silver with 0.1 *N* thiocyanate.

Procedure 2.[1] Pipet a 25 or 50 ml. sample of the chloride solution into a 250 ml. Erlenmeyer flask, and add 5 ml. of 6 *N* nitric acid. Add standard 0.1 *N* silver nitrate solution from a buret until an excess of 2 to 5 ml. is present. Then add 3 ml. of pure nitrobenzene and 1 ml. of ferric alum indicator and shake vigorously to coagulate the precipitate. Titrate the excess silver with standard 0.1 *N* potassium thiocyanate solution until a permanent reddish-brown color appears that does not fade after five minutes.

NOTES:

1. In the determination of bromide and iodide it is not necessary to filter off the silver halide before the back-titration of the silver (see p. 476). In the iodide determination the indicator should be added after the addition of excess silver nitrate, for otherwise the ferric iron will liberate iodine from the iodide.
2. The great advantage of the Volhard method is that it can be used for the volumetric halide determination in strongly acid media.
3. The procedure can be applied to the determination of anions whose silver salts are slightly soluble in water but which are soluble in acid, such

---

[1] J. R. Caldwell and H. V. Moyer, Ind. Eng. Chem., Anal. Ed. 7, 38 (1935).

as oxalate, phosphate, arsenate, chromate, and sulfide; these may be precipitated in neutral solution with an excess of silver nitrate. The silver is back-titrated after filtration, or the washed precipitate is dissolved in dilute nitric acid and the silver titrated with thiocyanate.

Most slightly soluble sulfides, such as those of lead, bismuth, zinc, manganese, nickel, and cobalt, react with silver nitrate to form silver sulfide quantitatively (see the list of solubility products, p. 64):

$$PbS + 2\,AgNO_3 \rightarrow Ag_2S + Pb(NO_3)_2.$$

The excess of silver can be back-titrated; or the silver sulfide can be washed, dissolved in nitric acid, and boiled until all the nitrogen oxides are expelled, and then titrated with thiocyanate.

Determination of cyanide in potassium cyanide.

Weigh out 0.35 to 0.4 g. of potassium cyanide (use extreme care in working with this salt; it is a deadly poison), dissolve in water, add 5 to 6 ml. of 6 *N* ammonia and 0.2 g. of potassium iodide, dilute to 100 ml., and titrate with 0.1 *N* silver nitrate solution until a permanent turbidity of silver iodide is obtained. The turbidity is best seen by viewing the liquid against a dark background.

$$\begin{aligned} Ag^+ + 2\,CN^- &\rightleftarrows Ag(CN)_2^- \text{ (quantitative at end point)} \\ Ag(CN)_2^- + Ag^+ &\rightleftarrows Ag[Ag(CN)_2] \\ Ag[Ag(CN)_2] + 2\,NH_3 &\rightleftarrows Ag(NH_3)_2^+ + Ag(CN)_2^- \\ Ag(NH_3)_2^+ + I^- &\rightleftarrows AgI + 2\,NH_3. \end{aligned}$$

Calculate the cyanide content of the sample.

NOTES:

1. The method given is used for the determination of cyanide and silver. Quite generally it is preferable to titrate silver with thiocyanate. However, the latter method cannot be directly applied to the determination of silver in silver halides, for example in photographic films. The silver in these insoluble salts may be determined by dissolving the sample in an excess of standard cyanide solution and back-titrating with standard silver nitrate according to the method given above.

2. The titration of cyanide with silver nitrate can be applied to the determination of cations which form complex cyanides. Zinc and nickel, for example, react with cyanide to form slightly soluble cyanides:

$$Ni^{++} + 2\,CN^- \rightleftarrows Ni(CN)_2 \text{ (or } Ni[Ni(CN)_4]?).$$

This cyanide dissolves in an excess of alkali cyanide, forming a stable complex:

$$Ni(CN)_2 + 2\,CN^- \rightleftarrows Ni(CN)_4^{=}.$$

The titration is carried out by using iodide as an indicator and adding standard potassium cyanide solution to the ammoniacal nickel solution until the opalescence due to silver iodide disappears. The end point is not reached exactly at the equivalence point. Therefore the cyanide solution must be standardized against a nickel solution under approximately the same conditions as in the actual determination. The method is used for the routine determination of nickel in steel; ferric iron can be made harmless by transforming it into a complex citrate.

Mercurimetry.

(For the theory of mercurimetric processes see p. 479.)

Preparation of 250 to 500 ml. of 0.1 N mercuric nitrate solution. Weigh out approximately the calculated amount of C. P. mercuric nitrate, and transfer to a volumetric flask. Add about 5 ml. of 6 *N* nitric acid, and make up to the mark with water.

Standardization of mercuric nitrate solution against standard thiocyanate.

(See p. 480.)

Procedure. Add 1 ml. of ferric alum indicator and 5 ml. of 6 *N* nitric acid to 25 to 40 ml. of 0.1 *N* mercuric nitrate solution, and titrate at a temperature not higher than 20° with standard 0.1 *N* thiocyanate solution until the color changes to brownish. The indicator blank is negligibly small. Calculate the normality of the mercury solution.

Notes:

1. The mercuric thiocyanate formed during the titration is slightly soluble but remains in solution by complex formation with mercuric ions:

$$\mathrm{Hg^{++} + 2\ CNS^- \rightleftarrows Hg(CNS)_2}$$
$$\mathrm{Hg(CNS)_2 + Hg^{++} \rightleftarrows 2\ Hg(CNS)^+.}$$

It also dissolves in an excess of thiocyanate solution with the formation of complex ions:

$$\mathrm{Hg(CNS)_2 + CNS^- \rightleftarrows Hg(CNS)_3^-}$$
$$\mathrm{Hg(CNS)_2 + 2\ CNS^- \rightleftarrows Hg(CNS)_4^{=}.}$$

The solution remains clear during the titration until near the equivalence point. Then there are not enough mercury ions left to keep the mercuric thiocyanate in solution, and the latter separates in the form of colorless needles. The precipitate does not interfere with the sharpness of the color change.

2. The reverse titration can be applied to the determination of thiocyanate. In this case standard mercuric nitrate solution is added to the disappearance of the red-brown coloration. The color begins to fade before the end point is reached; the gradual fading indicates the approach of the latter. The last change from the brownish tinge to colorless can be recognized quite distinctly.

3. The procedure described is a very accurate one for the determination of mercuric compounds. However, chloride and bromide interfere because their mercuric salts are also slightly dissociated. Therefore mercury cannot be titrated directly in mercuric chloride. In this case it is necessary to add a solution of the mercury salt to an excess of sodium hydroxide, filter off and wash the mercuric oxide, and dissolve it in nitric acid.

4. Mercuric cyanide is much less dissociated than mercuric thiocyanate. The presence of mercuric cyanide does not interfere in the mercury titration with thiocyanate. Use can be made of this fact in the determination of cyanide. A solution of the latter is added to a measured excess of standard mercuric solution:

$$\mathrm{Hg^{++} + 2\ CN^- \rightleftarrows Hg(CN)_2}$$

and the excess of mercuric ions is titrated with thiocyanate.

5. A solution of mercuric thiocyanate in alkali thiocyanate gives a slightly soluble crystalline precipitate with zinc:

$$Hg(CNS)_2 + 2\,CNS^- \rightleftarrows Hg(CNS)_4^=$$
$$Hg(CNS)_4^= + Zn^{++} \rightleftarrows ZnHg(CNS)_4.$$

Use is made of this fact in the volumetric determination of zinc. The precipitate is allowed to settle, and the excess of thiocyanate is titrated in an aliquot part of the supernatant liquid with standard mercury solution. Aluminum and ferric iron do not interfere; copper, bismuth, nickel, cobalt, manganese, ferrous iron, chromium, and chloride must be removed.[1]

Titration of chloride with standard mercuric nitrate.

The halogen ions, as we have seen (p. 479), react with mercuric ions to give slightly dissociated mercuric halides:

$$Hg^{++} + 2\,Cl^- \rightleftarrows HgCl_2.$$

Therefore, if mercuric ions are added to a chloride solution, the former are removed by the formation of slightly dissociated mercuric chloride. When the equivalence point has been reached, there is a sudden increase in the mercuric-ion concentration. Sodium nitroprusside can be used as an indicator; mercuric nitroprusside is only very slightly soluble, and the solution therefore becomes turbid as soon as an excess of mercury has been added.

It is necessary to determine the indicator blank at the end of the titration. This may be done as follows: From the amount of standard mercury solution used, the mercuric chloride concentration at the end point is calculated roughly (within 10 per cent). A mercuric chloride solution having the same concentration and volume as the solution titrated at the end point, and containing the same amount of indicator, is prepared. Standard mercuric nitrate solution is then carefully added to the synthetic solution until a turbidity appears. The blank is deducted from the volume of standard reagent used in the titration. The blank varies somewhat with the concentration of mercuric chloride at the end point, because part of the mercuric ions added in excess reacts with mercuric chloride, forming complex ions:

$$HgCl_2 + Hg^{++} \rightleftarrows 2\,HgCl^+.$$

The higher the concentration of mercuric chloride at the end point, the greater will be the number of mercuric ions removed by the complex formation, and consequently the larger the indicator blank will be. For a solution of 50 ml. of 0.05 N mercuric chloride, the correction amounts to 0.17 ml. of 0.1 N mercuric nitrate.

This titration method for chloride is of great practical importance, since it allows the direct determination of this anion *in acid medium even at great dilutions.* It deserves a much wider application than it enjoys at present.

Indicator solution: 10 per cent sodium nitroprusside. The solution should be kept in a dark bottle. 0.1 ml. is used for each 10 ml. of solution titrated.

---

[1] For a more detailed discussion see I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis*, Vol. II.

Procedure. Add the indicator to a measured volume of chloride solution, and titrate with standard mercuric nitrate until a permanent turbidity is obtained. Standardize the mercuric nitrate solution against pure sodium chloride under the same conditions as obtain in the titration. Determine the indicator blank as described above.

NOTES:

1. The presence of mineral acid has virtually no effect upon the results.
2. Bromides and thiocyanates may also be titrated in this way.
3. Of the metallic salts, those of copper, nickel, cobalt, and cadmium interfere because they form slightly soluble nitroprussides. Zinc, ferric iron, bismuth, manganese, aluminum, barium, calcium, strontium, and magnesium do not interfere in dilute solution.

Determination of zinc by precipitation with standard potassium ferrocyanide solution.

Zinc ions in neutral or acid medium react with potassium ferrocyanide to form extremely slightly soluble potassium zinc ferrocyanide:

$$2\,K_4Fe(CN)_6 + 3\,Zn^{++} \rightarrow K_2Zn_3[Fe(CN)_6]_2 + 6\,K^+.$$

This reaction has been used for more than sixty years for the determination of zinc. Until recently the end point was detected by means of external indicators such as uranyl nitrate, ammonium molybate, or ferric chloride. In general the first is the best external indicator. The acidified zinc solution was titrated at 40° with ferrocyanide. In the neighborhood of the end point a drop of the solution was brought in contact with a drop of 1 per cent uranium nitrate on a spot plate and the color observed after thirty seconds. A pale red-brown color (due to the formation of uranyl ferrocyanide) indicated the end point.

The proper use of an external indicator requires some skill, and it is therefore preferable to use an internal indicator whenever possible. As such, diphenylamine, diphenylbenzidine, or diphenylamine sodium sulfonate can be used (p. 493). We have seen that these substances are oxidation-reduction indicators. The oxidation potential of a ferro-ferricyanide solution is given by the equation (see p. 482):

$$E = E_o + 0.060 \log \frac{[Fe(CN)_6^{---}]}{[Fe(CN)_6^{----}]}. \quad (30°)$$

An acid solution of a mixture of ferro- and ferricyanide has an oxidation potential much lower than that required to oxidize the indicators to their intensely colored oxidation products. However, if zinc is added to the mixture, the ferrocyanide is precipitated as potassium zinc ferrocyanide. Since ferrocyanide is removed from the solution, the oxidation potential increases. After all of the ferrocyanide has reacted, there is a sharp rise in the oxidation potential; and the brilliant blue color of the oxidized form of the indicator develops with the slightest excess of zinc. The mathematical formulation of the process is somewhat complicated by the fact that zinc ferricyanide is also slightly soluble. Its solubility, however, is much greater than that of the ferrocyanide, so that the formation of zinc ferricyanide does not interfere with the color change.

It is also possible to titrate in the reverse manner. When diphenylamine is added to an acid solution of zinc containing a little ferricyanide, the blue-violet oxidation product is formed. This coloration will persist upon titration with ferrocyanide until all of the zinc has been transformed into potassium zinc ferrocyanide. The first excess of ferrocyanide reduces the violet form of the indicator to the colorless form. Use is made of this fact in the determination of zinc with ferrocyanide.

Standard solutions.

0.05 M potassium ferrocyanide. A C. P. product of $K_4Fe(CN)_6 \cdot 3\,H_2O$ is recrystallized from water and dried over a saturated solution of sodium bromide dihydrate to constant weight; it then consists of the trihydrate. The sample can also be dehydrated by heating at 100° to constant weight. A 0.05 molar solution is prepared and stabilized by the addition of 0.2 g. of sodium carbonate per liter. Standardize the solution against the standard zinc solution according to the procedure given below.

0.1 M standard zinc solution. An exactly weighed amount of pure zinc is dissolved in dilute sulfuric acid and diluted to the mark with water in a volumetric flask. The solution should be approximately 0.1 *M*. From the amount of zinc taken, the exact concentration is calculated.

Reagents: *Potassium ferricyanide solution.* 1 per cent solution of C. P. potassium ferricyanide in equilibrium water. It is kept in a dark bottle.

Indicator: 1 per cent solution of diphenylamine in concentrated sulfuric acid. Diphenylbenzidine and diphenylamine sodium sulfonate can be used, but a better end point is obtained with diphenylamine.

Procedure (*for standardization and zinc determination in an unknown solution*). To 25 ml. of zinc sulfate solution in a 250 ml. Erlenmeyer flask, add 25 to 75 ml. of water, 2 g. of ammonium sulfate, 10 to 30 ml. of 6 N H_2SO_4, 2 or 3 drops of the potassium ferricyanide solution, and 2 or 3 drops of diphenylamine indicator solution. Wait until the blue color develops, and titrate past the end point with 0.05 *M* potassium ferrocyanide solution until the blue color changes to a light, creamy yellowish-green. Diminish the speed of titration as the end point is approached, and do not add more than 1 to 2 ml. of ferrocyanide in excess. Back-titrate slowly with standard zinc solution to the appearance of the purple color. A sharp color change is produced by the addition of one drop of reagent. If the end point is overstepped, the excess of zinc can be back-titrated with the standard ferrocyanide solution. An indicator blank of 0.05 ml. of 0.05 *M* ferrocyanide for the 3 drops of indicator should be added to the volume used.

NOTES:

1. Iron and other metals which form insoluble ferrocyanides must be absent.
2. The appearance of the initial blue color is somewhat facilitated if a few ml. of ferrocyanide solution are added before the addition of the ferricyanide and indicator.

3. In order to obtain accurate results (within 0.3 per cent), the conditions under which the titration is carried out must be rigidly controlled and should be exactly the same as in the standardization. The speed of titration near the end point and the excess of ferrocyanide added before the back-titration with zinc must be kept uniform. The inaccuracy increases with the amount of ferrocyanide added in excess.

PROBLEMS

1. Indicate how chloride can be determined volumetrically in each of the following salts: calcium chloride, manganous chloride, barium chloride, ferric chloride, sodium chloride + sodium phosphate, sodium chloride + sodium sulfite, sodium chloride + sodium sulfate.

2. 0.2000 g. of a sample of zinc sulfide was treated with 50 ml. 0.1000 *N* silver nitrate. After complete transformation, the mixture was filtered, washed, and the excess of silver back-titrated with 15.50 ml. 0.1 *N* thiocyanate. Calculate the percentage of zinc sulfide in the sample. *Ans.* 84.04 per cent

3. When silver nitrate is added to a solution of Na_2HPO_4, a yellow precipitate of Ag_3PO_4 is formed. The precipitation can be made quantitative by adding enough sodium hydroxide (using phenolphthalein as indicator) to neutralize the acid formed. Write the equations. Show how this reaction may be made the basis of an argentimetric method for phosphate.

4. 0.3074 g. of a mixture of pure potassium chloride and pure potassium bromide required 30.98 ml. of 0.1007 *N* silver nitrate solution for titration. Calculate the percentage of potassium chloride and of potassium bromide in the mixture. *Ans.* 34.85 per cent KCl; 65.15 per cent KBr.

5. Devise a method for determining silver volumetrically in an alloy consisting of silver and nickel.

6. 0.3236 g. of a mixture of anhydrous silver halides was dissolved in 50.00 ml. of 0.1810 *M* potassium cyanide solution. The excess of cyanide required 28.14 ml. of 0.1010 *N* silver nitrate solution for back-titration. Calculate the silver content of the mixture. *Ans.* 56.13 per cent Ag.

7. How many ml. of 0.0510 *M* ferrocyanide solution are required to titrate 25.00 ml. of 0.1000 *M* zinc sulfate?

$$2\,K_4Fe(CN)_6 + 3\,Zn^{++} \rightarrow K_2Zn_3[Fe(CN)_6]_2 + 6\,K^+.$$

Ans. 32.7 ml.

8. A potassium chlorate solution is reduced in acid medium with sulfur dioxide to chloride (write reaction equation). After removal of the excess sulfur dioxide, 50.00 ml. of 0.1001 *N* silver nitrate are added, the precipitate is filtered off and washed, and the excess of silver is back-titrated with 20.35 ml. of 0.09982 *N* ammonium thiocyanate solution. (What indicator is used?) (a) Calculate the amount of potassium chlorate in the solution. (b) Would it be possible to titrate the chloride formed after reduction and removal of the excess of sulfur dioxide according to Mohr? (Chloride-free reagents may be added to the solution to reduce the acidity).

9. A sample consists of a mixture of alkali metal chloride and chromate. (a) How can one determine the chloride in this mixture by a direct titration? (b) Is it possible to determine the sum of chloride and chromate by an argentimetric titration?

10. To 100 ml. of a fresh solution of hydrogen sulfide in water are added 50.00 ml. of 0.1000 *N* silver nitrate. The precipitate is filtered off and washed. For the titration of the acid in the filtrate 38.50 ml. of 0.1015 *N* sodium hydroxide are required. (a) What indicator is used? (b) How many ml. of 0.0990 *N* thiocyanate would be required to titrate the excess of silver in the filtrate? (c) Calculate the molarity of the hydrogen sulfide solution.

CHAPTER XXXVI

REAGENTS USED IN OXIDATION–REDUCTION TITRATIONS

Oxidizing agents.

Potassium permanganate. This oxidizing agent was first used by Margueritte[1] for the well-known titration of ferrous iron and soon thereafter became a common reagent in the analytical laboratory. It is a strong oxidizing agent, its oxidation potential in 1 *N* sulfuric acid being of the order of 1.5 volts. In acid medium the reduction of permanganate can be represented by the following equation:

$$MnO_4^- + 8\ H^+ + 5\ e \rightarrow Mn^{++} + 4\ H_2O.$$

In feebly acid, neutral, or alkaline solutions the septavalent manganese is reduced to the quadrivalent state, thus causing the precipitation of hydrated manganese dioxide during the titration:

$$MnO_4^- + 2\ H_2O + 3\ e \rightleftarrows MnO_2 + 4\ OH^-.$$

In titrations of colorless or slightly colored solutions with permanganate it is not necessary to use an indicator, since an excess of the reagent is indicated by its color. One-tenth milliliter of 0.01 *N* permanganate imparts an extremely pale pink color to 100 ml. of water, and 0.2 ml. imparts a pale pink color; temperature and acid concentration are without influence upon the limit of visibility. Since the intensity of the color of oxidized diphenylamine, diphenylbenzidine, diphenylamine sulfonic acid (see p. 493), and the ferrous-phenanthroline complex is much greater than that of permanganate, the use of these indicators is recommended in titrations with very dilute permanganate, at least if the indicator is not attacked before the end point is reached.

In acid medium potassium permanganate reacts very rapidly with many reducing substances according to definite stoichiometric equations. There are, however, some practical disadvantages involved in the use of permanganate. In the first place, it is difficult to obtain potassium permanganate in an entirely pure state; it is generally contaminated by traces of manganese dioxide. Therefore a solution prepared by weighing out an exactly known amount of a C. P. product must be standardized. Moreover, ordinary distilled water is likely to contain reducing substances which will react with the permanganate to form manganese dioxide. Before using the solution, it is necessary to filter it through a non-reducing filter to remove the manganese dioxide. The presence of the latter is very objectionable because it catalyzes the auto-decomposition of permanganate on standing. If proper care is taken, manganese dioxide-free solutions of permanganate can be kept unchanged for a long time; acid solutions cannot be kept, since they decompose faster than neutral solutions, the dioxide formed again accelerating further decomposition.

---

[1] F. Margueritte, Compt. rend. *22*, 587 (1846).

Boiling permanganate solutions, especially if acid, are subject to auto-decomposition with the evolution of oxygen. Again this process is catalyzed by manganese dioxide. This fact must be considered in those cases in which a substance is oxidized in hot solution with an excess of permanganate (hypophosphite, phosphite, various organic substances), the latter being titrated back with a suitable reducing agent. It was found, for example, that on heating a 0.05 N potassium permanganate solution in 0.4 N sulfuric acid for one hour at 100° the loss by decomposition amounted to 0.6 per cent; in 0.8 N sulfuric acid, to 1.7 per cent; in 2 N acid, to 58 per cent. The decomposition is also appreciable in hot alkaline solution. In the back-titration of an excess of permanganate, an excess of a standard reducing agent (e.g., ferrous sulfate, oxalate) is usually added and the latter determined with the standard permanganate. The direct titration of permanganate with a reducing agent often gives rise to difficulties, since compounds of manganese intermediate between divalent manganese and permanganate are formed, imparting a brownish color to the solution. Complete decoloration to the manganous state then often occurs slowly.

Many titrations with permanganate, such as those of arsenic trioxide, trivalent antimony, hydrogen peroxide, and ferrocyanide, can be carried out in the presence of hydrochloric acid. This is not the case with the titration of ferrous iron. The reaction between ferrous iron and permanganate *induces* (see p. 498) the oxidation of hydrochloric acid by the permanganate, and hypochlorous acid or chlorine is formed. These oxidation products react incompletely with ferrous iron, and the result is the consumption of too much permanganate in the titration of iron in the presence of hydrochloric acid. Addition of a manganous salt is quite effective in preventing the induced oxidation of hydrochloric acid.

Ceric sulfate. Ceric sulfate was first used as an oxidizing agent by Lange[1] and later applied by various workers. It was not until after the systematic investigations of Willard and Young at the University of Michigan and of Furman and co-workers at Princeton University that ceric sulfate became a common reagent in the analytical laboratory. It can now be obtained in a fairly pure state in the form of the double salt, ceric ammonium sulfate. Ceric sulfate is a powerful oxidizing agent and is used in acid medium only.

$$Ce^{++++} + e \rightleftarrows Ce^{+++}.$$

The solution has an intense yellow color, and in solutions not too dilute the end point may be detected without the use of an indicator. In general, however, it is preferable to add a suitable indicator.

Ceric sulfate solutions have the advantage over permanganate that they are less subject to decomposition on standing and even on boiling. If oxidations must be carried out in acid solutions with an excess of oxidizing agent at boiling temperatures, it is preferable to use ceric sulfate instead of permanganate. Naturally the presence of chlorides interferes since they reduce the hot ceric cerium solution. Another advantage is that in the reduction of ceric cerium no intermediate products are formed. An advantage of ceric sulfate over permanganate is that the former can be used in the titration of ferrous iron in the presence of chloride.

Smith and Getz[2] claim that quadrivalent cerium in strongly acid medium is present in the form of a complex cerate ion. The oxidation potential of the cerium solution depends upon the concentration and kind of acid present. The "hexaperchlorato cerate" ion [$Ce(ClO_4)_6^{=}$] is the strongest oxidizing ion; it is reduced according to the equation:

$$Ce(ClO_4)_6^{=} + e \rightarrow Ce^{+++} + 6\,ClO_4^{-}.$$

Smith and Getz give the following oxidation potentials of cerium solutions in 1 to 8 N solutions of various acids:

perchloric acid	$Ce(ClO_4)_6^{=}$: 1.70–1.87 volts
nitric acid	$Ce(NO_3)_6^{=}$: 1.61–1.56 volts
sulfuric acid	$Ce(SO_4)_3^{=}$: 1.44–1.42 volts
hydrochloric acid	$CeCl_6^{=}$: 1.28 volts (decomposes in 1 N HCl)

---

[1] L. T. Lange, J. prakt. Chem. *82*, 129 (1861).

[2] G. F. Smith and C. A. Getz, Ind. Eng. Chem., Anal. Ed. *10*, 191 (1938).

Analytical use is made of the fact that solutions of cerium in perchloric or nitric acid are much stronger oxidizing agents than ceric sulfate solution in sulfuric acid.

Potassium dichromate. This salt can be obtained in a pure state by recrystallization from water and drying at 150° to 180°. Therefore standard solutions of exactly known content can be prepared by weighing out the pure dry salt and diluting to the proper volume. Potassium dichromate solutions do not change their titer on standing. The oxidation potential of dichromate in acid medium is less than that of permanganate or ceric cerium. In the reduction green chromic ions are formed, and therefore an indicator must be used for the detection of the end point:

$$Cr_2O_7^{=} + 14\ H^+ + 6\ e \rightarrow 2\ Cr^{+++} + 7\ H_2O.$$

Diphenylamine sulfonic acid, diphenylbenzidine, and diphenylamine are most useful; the ferrous-phenanthroline complex is less suitable since its oxidation potential is so high. A great practical advantage in the use of dichromate lies in the fact that ferrous iron can be titrated in the presence of hydrochloric acid; the latter is not oxidized provided that the acid concentration is less than 1 or 2 *N*.

Iodine. The oxidation potential of iodine is much lower than that of the oxidizing agents mentioned above (see table, p. 483); it is of the same order as that of the ferrous-ferric iron system. Iodine can be obtained in a pure state by sublimation, and standard solutions can be prepared by weighing out known amounts of the pure product. Iodine is only slightly soluble in water but dissolves readily in a potassium iodide solution with the formation of tri-iodide ions:

$$I_2 + I^- \rightleftarrows I_3^-.$$

Iodine is volatile even in potassium iodide solutions; an excess of iodide decreases the volatility because it displaces the equilibrium to the right in the above equation. In using standard iodine solutions, one should be careful in withdrawing the liquid not to expose the solution to the atmosphere for a longer time than is really necessary. Acid iodine solutions cannot be kept in storage because hydrogen iodide is easily oxidized by the air, resulting in an increase of the titer of the iodine solution.

Iodine in solution has an intense yellow color, and therefore titrations of 0.1 *N* or stronger solutions can be made without an indicator. As a rule, however, it is preferable to use starch, which forms a blue adsorption compound with iodine of great color intensity, as an indicator. In certain titrations use is made of the solvents chloroform and carbon tetrachloride, in which the iodine has an intense purple color, for the detection of the end point.

In determinations in which an excess of iodine is used, the excess being back-titrated after a certain time of standing, closed flasks must be employed in order to prevent losses of iodine by volatilization. Such determinations are made, as a rule, in glass-stoppered flasks called "iodine flasks."

Potassium iodate. By recrystallization from water and drying at 180°, potassium iodate is easily obtained pure. It is very useful in the extemporaneous preparation of an acid iodine solution of known concentration:

$$IO_3^- + 5\,I^- + 6\,H^+ \rightarrow 3\,I_2 + 3\,H_2O.$$

By adding an excess of iodide and acid to a standard iodate solution, an equivalent amount of iodine is obtained. In strong hydrochloric acid solution iodate is quantitatively reduced to iodine monochloride, according to Andrews.[1] If the concentration of hydrochloric acid at the end point is at least 3 N, iodate reacts quantitatively with the following reducing agents according to the equations:

$$2\,KI + KIO_3 + 6\,HCl \rightarrow 3\,KCl + 3\,ICl + 3\,H_2O$$
$$2\,I_2 + KIO_3 + 6\,HCl \rightarrow KCl + 5\,ICl + 3\,H_2O$$
$$As_2O_3 + KIO_3 + 2\,HCl \rightarrow As_2O_5 + ICl + KCl + H_2O$$
$$N_2H_4 + KIO_3 + 2\,HCl \rightarrow KCl + ICl + N_2 + 3\,H_2O$$
$$2\,SO_2 + KIO_3 + 2\,HCl + H_2O \rightarrow 2\,H_2SO_4 + ICl + KCl.$$

Instead of using high concentrations of hydrochloric acid, it is possible to work in 0.5 N sulfuric acid in the presence of hydrogen cyanide. R. Lang[2] showed that iodine cyanide is then formed:

$$IO_3^- + 2\,I^- + 3\,HCN + 3\,H^+ \rightarrow 3\,ICN + 3\,H_2O.$$

Although the "iodine cyanide" method yields excellent results, great care should be taken in its application since hydrogen cyanide is an extremely dangerous poison.

Potassium bromate. This is obtained in a pure state by recrystallization from water and drying at 180°. Bromate is a strong oxidizing agent in acid medium and is reduced to bromide, which finally reacts with the first excess of bromate to form free bromine:

$$BrO_3^- + 5\,Br^- + 6\,H^+ \rightarrow 3\,Br_2 + 3\,H_2O.$$

---

[1] L. W. Andrews, J. Am. Chem. Soc. *25*, 756 (1903); see especially G. S. Jamieson, *Volumetric Iodate Methods*, The Chemical Catalog Co., New York, 1926.

[2] R. Lang, Z. anorg. allgem. Chem. *122*, 332 (1922); *142*, 229, 279 (1925); *144*, 75 (1925); see also Kolthoff and Stenger, *Volumetric Analysis*, Vol. II.

Bromine may be detected by its yellow color; but its presence is shown much more sensitively by azo indicators, such as methyl red (sodium salt in water) and methyl orange. These indicators have a red color in acid medium but are destroyed by free bromine, thus giving a color change from red to pale yellow. The color change is not reversible, since the indicators are decomposed by the bromine. The reaction between bromine and the indicator proceeds rapidly, especially in strongly acid medium and at higher temperatures; since the color change is irreversible, there is a possibility that the bromate present in local excess may react with the indicator before the end point is reached. A fading of the color is often noticed before the end point is reached.

Smith and Bliss[1] tested a great number of dyes with regard to their suitability as indicators in bromate titrations. The following are very useful: Bordeaux (color index[2] number 88), chrysoidine R (number 21), naphthol blue black (number 246). They are used as 0.1 per cent solutions in water. Indigo sulfonic acids may also be used as indicators; the blue color is destroyed by bromine.

Direct titration with bromate is of special advantage in the determination of trivalent arsenic and antimony, of thallous thallium, and of hydrazine in acid medium:

$$BrO_3^- + 3\,As^{+++} + 6\,H^+ \rightarrow Br^- + 3\,As^{+++++} + 3\,H_2O$$

$$3\,N_2H_4 + 2\,BrO_3^- \rightarrow 2\,Br^- + 3\,N_2 + 6\,H_2O.$$

Various substances cannot be oxidized directly with bromate but react quantitatively with an excess of bromine. Acid solutions of bromine of exactly known concentration are obtained from a standard bromate solution by adding an excess of bromide and acid:

$$BrO_3^- + 5\,Br^- + 6\,H^+ \rightarrow 3\,Br_2 + 3\,H_2O.$$

Bromine is very volatile, and therefore such operations with an excess of bromine must be carried out in iodine flasks or in tightly stoppered glass bottles at as low a temperature as possible. The excess of bromine is determined iodometrically (addition of potassium iodide and titration with thiosulfate) or by the quick addition of an excess of standard arsenious oxide, which is then back-titrated with standard bromate.

An important use is made of bromate in organic analysis. Substances with a phenol group react with bromine to form brominated substitution products. Ordinary phenol, for example, reacts with an excess of bromine with the formation of tribromophenol bromide, which upon back-titration of the excess of bromine (iodometrically or with arsenious oxide) is transformed into tribromophenol:

---

[1] G. F. Smith and H. H. Bliss, J. Am. Chem. Soc. *53*, 2091 (1931).

[2] Society of Dyers and Colorists, *Colour Index*.

$$C_6H_5OH + 3\,Br_2 \rightarrow C_6H_2Br_3OH + 3\,H^+ + 3\,Br^-.$$

The well-known method of Koppeschaar[1] for the titration of phenols is based on this reaction.

An important use of this method is made in the determination of various metals which form insoluble compounds of definite composition with 8-hydroxyquinoline (see p. 79). 8-Hydroxyquinoline (sometimes called *oxine*) yields a dibromo substitution product with bromine:[2]

$$C_9H_7ON + 2\,Br_2 \rightarrow C_9H_5Br_2ON + 2\,H^+ + 2\,Br^-.$$

The application of the method for the determination of magnesium is described on page 638.

Calcium hypochlorite. One-tenth normal solutions of calcium hypochlorite are quite stable. Hypochlorite is a powerful oxidizing agent and is of special advantage in oxidations carried out in neutral or alkaline medium. It reacts fairly rapidly with various substances which are not at all or only slowly oxidized in acid medium by other common oxidizing agents such as permanganate and ceric sulfate.

In many cases hypobromite reacts faster than hypochlorite; a hypobromite solution of known concentration can be prepared extemporaneously by adding an excess of alkali bromide to a standard hypochlorite solution:

$$OCl^- + \underset{(excess)}{Br^-} \rightarrow OBr^- + Cl^-.$$

Usually an excess of hypochlorite (or hypobromite) is used in oxidations. The excess can be determined iodometrically by adding an excess of potassium iodide and acid and titrating the liberated iodine with sodium thiosulfate:

$$OCl^- + 2\,I^- + 2\,H^+ \rightarrow I_2 + Cl^- + H_2O$$
$$2\,S_2O_3^= + I_2 \rightarrow S_4O_6^= + 2\,I^-.$$

For the back-titration one can also add an excess of standard arsenious oxide solution and titrate the excess with standard hypochlorite or bromate, using Bordeaux as indicator (see p. 586).

$$2\,OCl^- + As_2O_3 \rightarrow As_2O_5 + 2\,Cl^-.$$

In bicarbonate medium ammonia is quantitatively oxidized by hypobromite according to the equation

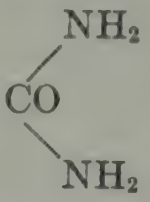
$$2\,NH_3 + 3\,OBr^- \rightarrow N_2 + 3\,Br^- + 3\,H_2O.$$

---

[1] W. F. Koppeschaar, Z. anal. Chem. *15*, 233 (1876).

[2] R. Berg, Pharm. Zeitg. *71*, 1542 (1926).

This reaction is made the basis of an exact method for the determination of ammonia. Urea is oxidized in bicarbonate medium to nitrogen. carbon dioxide, and water:



$$CO(NH_2)_2 + 3\,OBr^- \rightarrow CO_2 + N_2 + 2\,H_2O + 3\,Br^-.$$

In alkaline medium sulfide, thiosulfate, and tetrathionate are quantitatively oxidized to sulfate:

$$S^= + 4\,OCl^- \rightarrow SO_4^= + 4\,Cl^-$$
$$S_2O_3^= + 4\,OCl^- + H_2O \rightarrow 2\,SO_4^= + 4\,Cl^- + 2\,H^+.$$

Nitrite in weakly alkaline medium is oxidized to nitrate:

$$NO_2^- + OCl^- \rightarrow NO_3^- + Cl^-.$$

This reaction furnishes one of the best methods for the determination of nitrites.

Finally, it may be mentioned that hydrogen peroxide in weakly alkaline medium behaves as a reducing agent towards hypochlorite or hypobromite. The reaction proceeds quantitatively according to the equation

$$OCl^- + H_2O_2 \rightarrow H_2O + O_2 + Cl^-.$$

Reducing agents.

Standard solutions of reducing agents are used in the titration of oxidizing agents. Most of these reducing agents are not air-stable, since they are slowly oxidized by the oxygen of the air. Standard solutions of strong reducing agents such as titanous chloride or sulfate, or chromous chloride, must be protected from the oxygen of the air; and titrations must be made in an inert atmosphere of oxygen-free hydrogen, nitrogen, or carbon dioxide. In contact with the air they are rapidly oxidized, especially during a titration. Titanous chloride and chromous chloride are valuable reagents. On account of the great care required in their use, they are not employed as ordinary laboratory standard solutions but find application in routine analyses.

Ferrous salts. Solutions of ferrous salts are slowly oxidized by air. This air oxidation is relatively rapid in neutral medium but is inhibited by an excess of acid. A maximum stability is found in solutions containing 0.5 to 1 N sulfuric acid. But even such solutions must be standardized daily.

Standard ferrous iron solutions are often used in the determination of oxidizing substances. In many cases the reaction is sufficiently rapid to enable the titration to be made directly to the end point, using one of the suitable oxidation-reduction indicators (p. 492). Acid solutions of ceric sulfate, dichromate, and vanadate can be titrated directly with a ferrous iron solution. In the titration of permanganate a slight excess of ferrous iron is added and the latter back-titrated, since the direct titration does not proceed smoothly. Various oxidizing substances react slowly with ferrous iron; this, for example, is the case with lead peroxide minium, pyrolusite (MnO_2), and nitric acid, the latter in strongly acid medium:

$$MnO_2 + 2\,Fe^{++} + 4\,H^+ \rightarrow Mn^{++} + 2\,Fe^{+++} + 2\,H_2O$$
$$NO_3^- + 3\,Fe^{++} + 4\,H^+ \rightarrow NO + 3\,Fe^{+++} + 2\,H_2O.$$

The latter reaction is catalyzed by molybdate.[1]

In such cases the oxidizing substance to be determined is heated with an excess of standard ferrous iron solution until the reaction is complete. However, solutions of ferrous iron are air-sensitive, especially at higher temperatures; and therefore it is necessary in the above cases to protect the mixtures containing excess ferrous iron from air oxidation. This can be accomplished by displacing the air in the reaction vessel by an inert gas, such as carbon dioxide or oxygen-free nitrogen, and passing the gas through the solution during the entire procedure. As a rule it is possible to get satisfactory results in a much simpler way by attaching a *Contat-Göckel trap* to a flask containing the solution (Fig. 115), or by use of the arrangement depicted in Figure 116.

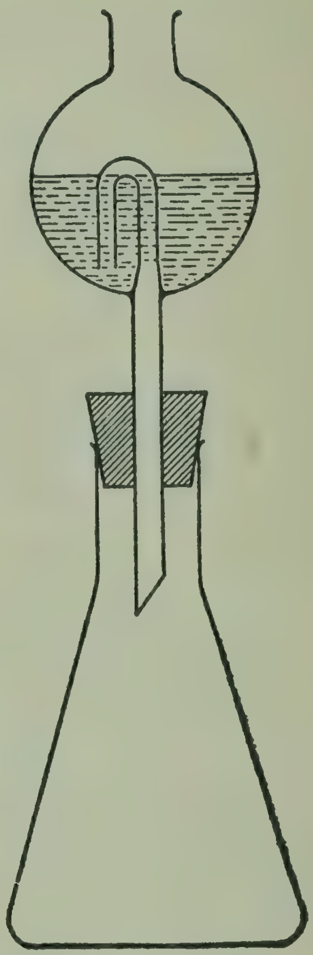


FIG. 115. Flask with Contat-Göckel trap.

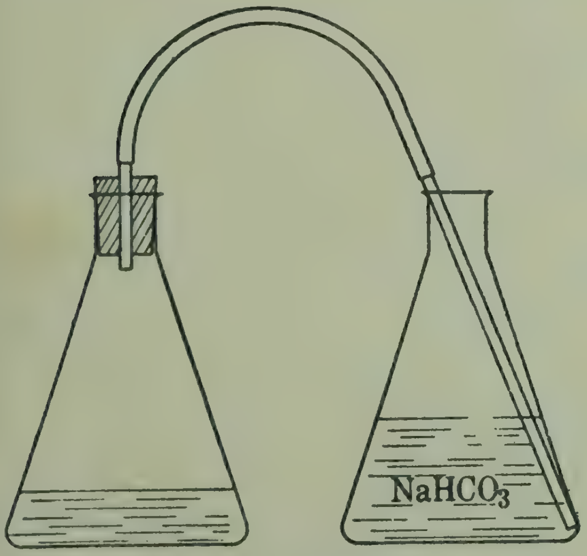


FIG. 116. Arrangement for excluding air from an acid solution.

The *Contat-Göckel*[2] *trap* is filled with sufficient water or sodium bicarbonate solution to cover the end of the siphon tube. At the end of the boiling the trap is filled about half-full of saturated sodium bicarbonate or 20 per cent potassium bicarbonate solution. As the flask cools, the solution is automatically drawn in until the pressure of the carbon dioxide in the flask is equal to the external pressure; the bicarbonate in the trap protects the contents of the flask from the oxygen of the air. The apparatus of Figure 116 is used in a similar way. The apparatus is also useful in other cases when solutions must be protected from air oxidation after complete reduction ($Sn^{IV} \rightarrow Sn^{II}$; $Ti^{IV} \rightarrow Ti^{III}$, etc.).

---

[1] For a volumetric nitrate determination based on the reduction of an excess of ferrous iron, see I. M. Kolthoff, E. B. Sandell, and B. Moskovitz, J. Am. Chem. Soc. *55*, 1454 (1933).

[2] A. Contat, Chem. Ztg. *22*, 298 (1898); H. Göckel, Z. angew. Chem. *13*, 620 (1899).

Sodium thiosulfate. Sodium thiosulfate is the most important reagent used in iodometry. Solutions prepared from a pure salt in pure water (conductivity water) are quite stable. However, if the water contains an excess of carbon dioxide, a slow decomposition takes place:

$$S_2O_3^{=} + H^+ \rightarrow HSO_3^- + S,$$

with the formation of some sulfur.

Thiosulfate is slowly oxidized by oxygen of the air; sulfite is slowly formed and is then rapidly oxidized to sulfate:

$$\begin{array}{l} S_2O_3^{=} \rightarrow SO_3^{=} + S \text{ (very slow)} \\ \underline{SO_3^{=} + \tfrac{1}{2}\,O_2 \rightarrow SO_4^{=} \text{ (measurable)}} \\ S_2O_3^{=} + \tfrac{1}{2}\,O_2 \rightarrow SO_4^{=} + S. \end{array}$$

There is also a possibility of the intermediate formation of tetrathionate. This is especially the case in the presence of copper, which strongly catalyzes the decomposition of thiosulfate:

$$2\,Cu^{++} + 2\,S_2O_3^{=} \rightarrow 2\,Cu^+ + S_4O_6^{=} \text{ (instantaneous)}$$
$$2\,Cu^+ + \tfrac{1}{2}\,O_2 + 2\,H^+ \rightarrow 2\,Cu^{++} + H_2O \text{ (measurable).}$$

Ordinary distilled water often contains traces of copper derived from the storage system. Since the copper has a detrimental effect upon the stability of thiosulfate, it is desirable to use water free from this metal for preparing the solution. In addition, it is best to add 0.1 per cent of sodium carbonate as a preservative to the freshly prepared thiosulfate solution. The sodium carbonate has two functions: It makes harmless any carbon dioxide present in the water (acid decomposition of thiosulfate, see above) and removes copper ions, if present.

Even with the above-mentioned precautions it is necessary to restandardize a thiosulfate solution after it has stood for some time. The entire mechanism of its decomposition is extremely complicated. In addition to these causes of slow decomposition, a deterioration may occur as a result of the growth of microörganisms (thiobacteria). Organisms that consume sulfur apparently exist in the atmosphere; and these can withdraw sulfur from thiosulfate, converting it into sulfite, which in turn is easily oxidized to sulfate by air. If a decomposition by microörganisms occurs, a strong turbidity is usually noticed on long standing, and the titer of the solution decreases fairly rapidly. In such cases it is best to discard the solution and prepare a new one, which is kept in a bottle cleaned with cleaning mixture.

In some texts the stabilization of thiosulfate solutions by the addition of sodium hydroxide is recommended. This procedure should not be followed; under such conditions an increase in the titer of the thiosulfate due to the formation of sulfite and sulfide may occur.

Arsenic trioxide. This substance can be obtained relatively easily in a pure form and is valuable in the standardization of iodine solutions in bicarbonate medium. It also finds use in the titration of bromate or hypochlorite. The trioxide dissolves very slowly in water but readily in sodium hydroxide. A standard solution is usually prepared by dissolving a weighed amount of the pure substance in an excess of sodium hydroxide and adding hydrochloric acid until the reaction is neutral or slightly acid to litmus paper. An alkaline solution of the arsenic trioxide should not be kept, because arsenite is slowly oxidized to arsenate by air under these conditions, thus causing a decrease in the normality. Neutral or weakly acid solutions, on the other hand, are quite stable and can be kept unchanged for long periods of time.

Sodium oxalate and oxalic acid ($H_2C_2O_4 \cdot 2\,H_2O$). Both substances can be obtained in a pure state and are used in the standardization of permanganate and ceric sulfate. In addition, sodium oxalate is an excellent primary standard for the standardization of acids (see p. 549), and oxalic acid for bases. Solutions of oxalates and oxalic acid decrease in strength on standing, especially when exposed to light. A slow decomposition takes place:

$$H_2C_2O_4 \rightarrow CO_2 + CO + H_2O.$$

Standard solutions of sodium oxalate and oxalic acid should be kept in the dark, preferably in resistant glass bottles. Solutions of the acid can be kept unchanged under these conditions for more than a year; solutions of the sodium salt, however, are much less stable.

Potassium ferrocyanide ($K_4Fe(CN)_6 \cdot 3\,H_2O$). This salt is easily obtained in a pure state by recrystallization from water. It can be kept as the trihydrate over deliquescent sodium bromide, or it can be converted into the anhydrous form by drying at 110°. Its aqueous solutions are not very stable; an air oxidation takes place and, in addition, a decomposition catalyzed by light. Acids (carbon dioxide in the water) catalyze the decomposition very strongly. It is therefore best to add 0.2 per cent of sodium carbonate to the freshly prepared solution. If kept in a dark bottle, it is stable for more than a month, although restandardization at frequent intervals is recommended. Potassium ferrocyanide is a valuable standard for ceric sulfate. It is also of practical importance in the titration of zinc (for procedure see p. 577).

CHAPTER XXXVII

PERMANGANIMETRIC METHODS

Preparation of 0.1 *N* potassium permanganate.

Since distilled water usually contains traces of reducing substances which react slowly with permanganate to form hydrous manganese dioxide, it is necessary to remove these oxidizable substances to prepare a stable potassium permanganate solution, because finely divided manganese dioxide promotes the autodecomposition of permanganate (p. 582). This is most simply accomplished by boiling the solution for some time, cooling, and filtering off the manganese dioxide.

Dissolve about 3.2 g. of C. P. potassium permanganate in 1 liter of water, heat the solution to boiling, and keep slightly below the boiling point for an hour. Alternatively, allow the solution to stand at room temperature for two or three days. Filter the liquid through pure asbestos (free from organic matter) or through a sintered-glass filter crucible. Transfer the filtrate to a clean glass-stoppered bottle freed from grease with cleaning mixture. Protect the solution from evaporation, dust, and reducing vapors, and keep it in the dark or in diffuse light. If in time manganese dioxide settles out, refilter the solution and restandardize it.

If 0.01 *N* permanganate is required, it is prepared by dilution of 0.1 *N* solution with a good grade of water. The dilute solution should be prepared just before use and should not be stored for any length of time, because of the relatively rapid rate of deterioration.

Standardization. Standard substances.

Sodium oxalate, $Na_2C_2O_4$. ***Crystallized oxalic acid***, $H_2C_2O_4 \cdot 2\,H_2O$. In acid medium oxalic acid is oxidized by permanganate to carbon dioxide and water:

$$5\,C_2O_4^{=} + 2\,MnO_4^{-} + 16\,H^{+} \rightarrow 10\,CO_2 + 2\,Mn^{++} + 8\,H_2O.$$

For the purity of these standard substances compare page 549 and page 554.

Procedure. Weigh out 0.25 to 0.30 g. of pure sodium oxalate, dried at 105° to 110°, into a 250 ml. Erlenmeyer flask, dissolve in

60 ml. of water, add 15 ml. of 1 : 8 sulfuric acid (free from reducing substances), heat to 80° to 90°, and titrate slowly with permanganate to the first faint permanent pink tinge, swirling the solution constantly and being careful to wait until the solution is colorless before adding further amounts of permanganate. The temperature of the solution should be above 60° at the end point. Calculate the normality of the permanganate.

NOTES:

1. The mechanism of the reactions between oxalate and permanganate ions is extremely complicated.[1] The first few drops of permanganate react slowly with the oxalic acid; but after a small amount of manganous salt has been formed, the reaction occurs almost instantaneously in hot solution. It appears that the manganous ions catalyze the reaction between permanganate and oxalic acid. That this is true can be shown by adding a small amount of manganous salt at the very start of the titration; the permanganate is then reduced rapidly from the start.

In the titration of hydrogen peroxide with permanganate, a similar phenomenon is observed. The first few drops of permanganate are decolorized slowly, but again the reaction is catalyzed by adding a trace of a manganous salt at the very beginning of the titration.

2. A peculiar induced air oxidation takes place during the titration of oxalic acid with permanganate. In the presence of oxygen, part of the oxalic acid is oxidized to percarbonic acid, which then decomposes into hydrogen peroxide and carbon dioxide. At the end point all of the hydrogen peroxide has disappeared, because it is quantitatively oxidized by permanganate to water and oxygen. This side reaction has no influence upon the results, since 1 mole of oxalic acid requires 2 equivalents of oxidizing agent, and 1 mole of hydrogen peroxide formed from 1 mole of oxalic acid requires the same number.

3. Hot solutions of oxalic acid decompose slowly:

$$H_2C_2O_4 \rightarrow CO_2 + CO + H_2O.$$

This reaction is catalyzed by manganous salts, but it occurs only to a negligibly small extent if the titration is carried out according to the standard procedure. Too much permanganate, on the other hand, may be used as a result of the auto-decomposition of permanganate. In hot acid solution the latter is slowly decomposed with evolution of oxygen, and therefore too rapid titration and insufficient stirring of the liquid may lead to error.[2]

4. In the presence of hydrochloric acid, too much permanganate may be used, owing to an induced oxidation of chloride by the reaction between oxalic acid and permanganate. The error is eliminated by the addition of manganous salt. If the titration is made at temperatures above 70°, hydrochloric acid does not interfere[3] even in the absence of manganous salt.

5. The correction for the excess of permanganate required to give a visible color in the titrated solution may be obtained as follows. Cool the titrated

---

[1] For details cf. I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis*, Vol. II.

[2] See especially the extensive studies of R. S. McBride, J. Am. Chem. Soc. *34*, 393 (1912).

[3] G. P. Baxter and J. E. Zanetti, Am. Chem. J. *33*, 500 (1905).

solution to room temperature, add 0.1 g. of solid potassium iodide and 1 to 2 ml. of 0.5 per cent starch solution, and titrate slowly with 0.01 *N* sodium thiosulfate solution to the disappearance of the blue color. Obtain the ratio between the permanganate and thiosulfate solutions by running 2 to 3 ml. of 0.1 *N* permanganate solution into 50 ml. of 1 *N* sulfuric acid containing 0.1 g of potassium iodide and titrating the liberated iodine with the 0.01 *N* thiosulfate solution, using starch as indicator.

6. To avoid errors caused by decomposition at higher temperatures, Fowler and Bright[1] recommend the following procedure for the standardization at lower temperatures. They found results which were in close agreement with the theoretical value.

Procedure according to Fowler and Bright: Transfer 0.3 g. of sodium oxalate (dried at 105°) to a 600 ml. beaker. Add 250 ml. of diluted sulfuric acid (5 H_2SO_4 to 95 water) previously boiled for ten to fifteen minutes and then cooled to 27 ± 3°. Stir until the oxalate has dissolved. Add 39 to 40 ml. of 0.1 *N* permanganate (theoretical for 0.1 *N* is 44.73 ml.) at a rate of 25–35 ml. per minute while stirring slowly. Let stand until the pink color disappears. Heat to 55° to 60° and complete the titration by adding the permanganate until a faint color persists for thirty seconds. Add the last 0.5 to 1 ml. dropwise with particular care to allow each drop to become decolorized before the next is introduced.

If necessary determine the excess of permanganate required to impart a pink color to the solution by comparing with a blank containing the same amount of sulfuric acid at the same temperature as the solution titrated at the end point.

7. We have found that C. P. sodium oxalate usually contains some sodium carbonate or bicarbonate. Even the Bureau of Standards product was found to contain 0.1 per cent of sodium carbonate.

Other standard substances.

Arsenious oxide, As_2O_3 (see p. 622).

$$5\,As_2O_3 + 4\,MnO_4^- + 12\,H^+ \rightarrow 5\,As_2O_5 + 4\,Mn^{++} + 6\,H_2O.$$

Arsenious oxide is easily obtainable in a pure state (Bureau of Standards product is 99.97 per cent pure). Under the proper conditions the reaction between arsenious oxide and permanganate proceeds smoothly without side reactions. Therefore, *the authors prefer the use of arsenious oxide as a standard substance to that of sodium oxalate.* The titration of arsenious oxide with permanganate in sulfuric acid medium proceeds smoothly at the beginning, but a yellow-green or brown coloration soon appears (complex manganic arsenates) and disappears only slowly, even at high temperatures. If made in hot solution in the presence of hydrochloric acid, the titration may be carried out directly. It is better, however, to add a catalyst to accelerate the reaction between arsenious oxide and permanganate. A trace of iodate or iodide is a suitable catalyst.

---

[1] R. H. Fowler and H. A. Bright, J. Research Nat. Bur. Standards *15*, 493 (1935).

Procedure. Weigh out 0.2 to 0.25 g. of pure arsenious oxide, dissolve in 10 ml. of 3 *N* sodium hydroxide (free from reducing substances), add 15 ml. of 1:1 hydrochloric acid, dilute with 50 ml. of water, add 1 drop of 0.002 *M* potassium iodate, and titrate with permanganate to the first rose color.

NOTE: This titration is accurate to within 0.02 per cent. If ferrous-phenanthroline is used as indicator, the end point coincides with the equivalence point.[1]

Mohr's salt, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6\,H_2O$. Although Mohr's salt has a high reaction weight and the iron titration with permanganate is accurate and simple, the salt has the disadvantage of usually being contaminated with manganese, zinc, and magnesium. These metals can occur in the form of double ammonium sulfates isomorphous with Mohr's salt, and they cannot then be removed by recrystallization of the salt from water or precipitation from an aqueous solution with alcohol (cf. p. 165).

Mohr's salt, therefore, cannot be relied upon as a primary standard substance. Considering, however, its high equivalent weight and the simplicity of the procedure of standardization, it is sometimes advantageous to have available a large sample of Mohr's salt of *known activity* towards permanganate and to keep it in well-closed bottles in order to prevent efflorescence and oxidation of the ferrous iron. The salt should have a uniform green color.

Procedure. Weigh out 1.2 g. of the salt, dissolve in 50 ml. of 1 *N* sulfuric acid, add 5 ml. of 85 per cent phosphoric acid, and titrate to the first permanent pink.

Potassium iodide, KI. This substance can be prepared in a pure state and has been found very useful as a primary standard for silver nitrate,[2] potassium permanganate, and ceric sulfate.[3] The standardization of permanganate is done potentiometrically or according to Andrews [4] in 4 *N* hydrochloric acid (see p. 585) or by the iodocyanide method of Lang [5] (see p. 585).

Titrations with permanganate.

Iron. The titration of ferrous iron with permanganate is a simple matter. The solution is acidified with sulfuric acid and titrated directly to the end point. The color change is somewhat sharper if some 85 per cent phosphoric acid is added. The latter forms a colorless complex with ferric iron, and the color change therefore takes place from colorless to pink, whereas the change is from yellow to pinkish in the absence of phosphoric acid. Hydro-

[1] I. M. Kolthoff, H. A. Laitinen, and J. J. Lingane, J. Am. Chem. Soc. *59*, 429 (1937).

[2] Compare I. M. Kolthoff and J. J. Lingane, J. Am. Chem. Soc. *58*, 1524 (1936).

[3] I. M. Kolthoff, H. A. Laitinen, and J. J. Lingane, *loc. cit.*

[4] L. W. Andrews, *ibid. 25*, 756 (1903).

[5] R. Lang, Z. anorg. allgem. Chem. *122*, 332 (1922).

fluoric acid has the same effect as phosphoric acid; however, it etches the wall of the flask and is therefore not used unless its presence is required (p. 746). In the latter case the titration should be made in the absence of air, since hydrofluoric acid accelerates the oxidation of ferrous iron by oxygen. Chloride interferes in the iron titration. It has already been mentioned (p. 582) that the reaction between ferrous iron and permanganate induces the oxidation of hydrochloric acid to hypochlorous acid or chlorine. Therefore high results are found in the presence of chloride, and the end point is not permanent. Chloride is made practically harmless by the presence of a manganous salt, which is added in the form of the so-called Zimmermann-Reinhardt solution (p. 601), and by slow titration. However, under these conditions the titration is not highly accurate in the presence of *much* hydrochloric acid. The end point is fleeting since an excess of permanganate oxidizes the chloride slowly. Even with the use of the Zimmermann-Reinhardt mixture it is often advisable to remove most of the hydrochloric acid by evaporation.

The titration of ferrous iron is often required in the indirect determination of strong reducing agents. Solutions of stannous tin, titanous titanium, and cuprous copper, for example, can be titrated *directly* with permanganate in a current of carbon dioxide or nitrogen. These strong reducing substances are easily oxidized by the air, and therefore precautions must be taken to protect them from air oxidation. This air oxidation may be prevented by adding an excess of ferric iron to the solution immediately after the reduction of these metals to their lower valence states.

$$2\,Fe^{+++} + Sn^{++} \rightarrow 2\,Fe^{++} + Sn^{++++}$$
$$Fe^{+++} + Cu^{+} \rightarrow Fe^{++} + Cu^{++}$$
$$Fe^{+++} + Ti^{+++} \rightarrow Fe^{++} + Ti^{++++}.$$

An equivalent amount of ferrous iron is formed, which may be titrated with permanganate or any other suitable oxidizing agent (potassium dichromate, ceric sulfate) in the presence of air.

The reduction of ferric iron is also involved in the determination of hydroxylamine. In boiling acid solution the latter reduces ferric iron according to the equation[1]

$$2\,NH_2OH + 4\,Fe^{+++} \rightarrow N_2O + 4\,Fe^{++} + H_2O + 4\,H^{+}.$$

Reduction of ferric to ferrous iron. Iron very often occurs in the ferric form or as a mixture of ferric and ferrous iron. If all of the iron is to be determined oxidimetrically, the ferric iron must first be quantitatively reduced to the ferrous form. The excess of reducing agent must then be removed, or made harmless before the titration. A number of substances are suitable for the reduction of ferric iron.[1]

---

[1] W. C. Bray, M. E. Simpson, and A. A. MacKenzie, J. Am. Chem. Soc. *41*, 1363 (1919).

(1) Hydrogen sulfide and sulfurous acid, the excess of which can be removed by boiling, with protection of the ferrous iron solution against air oxidation (p. 589).

(2) Hydrogen with platinum black or platinized platinum gauze as catalyst. This method is hardly ever applied.

(3) Metals, such as zinc, cadmium, aluminum, silver (p. 498), and others which quantitatively reduce ferric iron to the ferrous state:

$$2\,Fe^{+++} + Zn \rightarrow 2\,Fe^{++} + Zn^{++}.$$

(4) Stannous chloride solution, which reduces ferric iron rapidly and the excess of which can be destroyed by oxidation to the stannic form by mercuric chloride:

$$2\,Fe^{+++} + Sn^{++} \rightarrow 2\,Fe^{++} + Sn^{++++}$$
$$Sn^{++} + 2\,HgCl_2 \rightarrow Hg_2Cl_2 + Sn^{++++} + 2\,Cl^-.$$

Of the methods mentioned, those involving the use of metals or stannous chloride are generally employed.

Reduction with metals. The Jones reductor. Zinc is the metal most frequently used as reducing agent. It can be purchased in a pure state but should always be tested for the presence of iron. This can be done by dissolving about 10 g. in 100 ml. of 1 : 5 sulfuric acid and adding 1 to 2 drops of 0.1 N permanganate. The solution should become distinctly colored. Instead of zinc, cadmium and aluminum are often used. All three of these can be used in the form of wire wound in a spiral or a chain which can be easily removed from the solution after the reduction is complete. Cadmium is obtainable in an iron-free state; aluminum as a rule contains a trace of iron and is therefore less suitable. It is possible of course to run a blank on the latter metal, but this is not very convenient. Then one must determine the amount of aluminum dissolved in order to apply the proper correction.

Very pure zinc and cadmium react rather slowly with acids. The presence of traces of other metals such as lead and copper accelerates the reaction markedly. However, these promote the solution of the metals in acid as well, and large quantities are lost by this simultaneous dissolution process. This can be prevented by the use of amalgamated metals. By treating zinc or cadmium with a dilute solution of a mercuric salt, the metal is covered with a layer of mercury, since the latter metal is lower in the electromotive series than zinc and cadmium:

$$Hg^{++} + Zn \rightarrow Zn^{++} + Hg.$$

In the discussion of electrolytic separations we saw that hydrogen has a high overvoltage at a mercury surface (see p. 152), which explains the fact that during the reduction of the ferric iron in acid solution little hydrogen is formed.

---

[1] For the interference of other substances which may be reduced with the iron, thus leading to high results, see p. 740.

Reduction with amalgamated zinc is usually carried out in the Jones reductor,[1] which consists of a column of amalgamated granulated zinc contained in a glass tube provided with a stopcock, through which the solution to be reduced may be drawn. Because of the large surface exposed, such a zinc column is much more efficient than pieces of zinc placed in the solution.

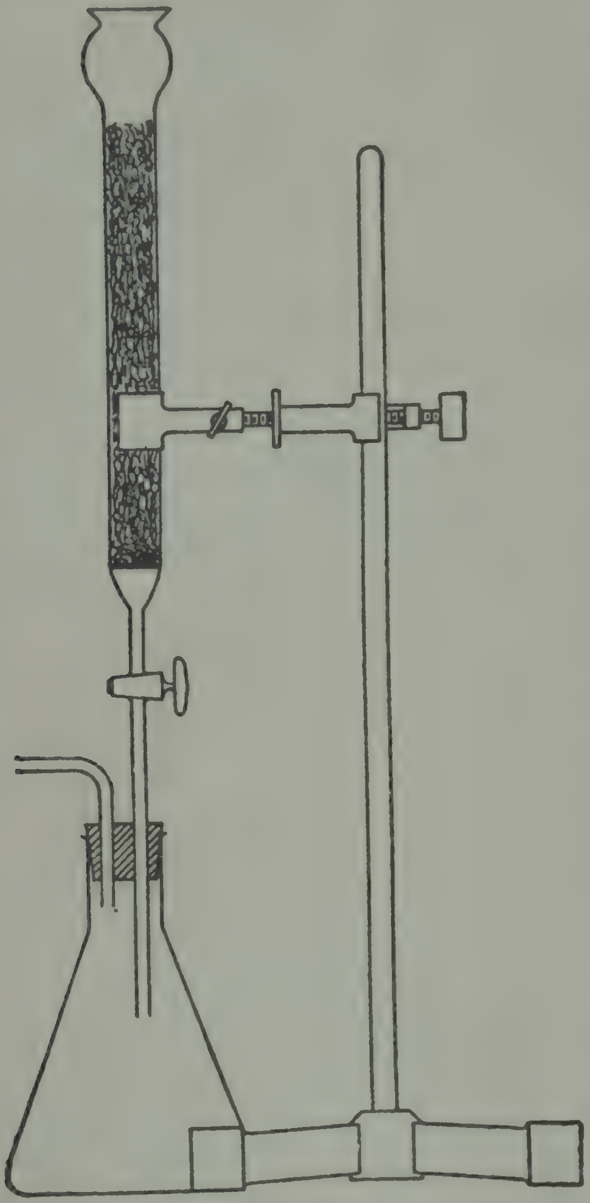


FIG. 117. Jones reductor.

A convenient form of the reductor is shown in Figure 117. The tube should be of sufficient length to hold a column of zinc 25 to 35 cm. in height and should have an internal diameter of approximately 2 cm. The zinc column rests on a pad of glass wool which is supported by a perforated porcelain plate; the top of the column should extend to within a short distance of the bottom of the upper reservoir. The outlet tube is connected to a 500 ml. Erlenmeyer flask by means of a two-hole rubber stopper, the second hole of which is provided with a bent glass tube for connection to the suction line.

Amalgamated zinc for use in the reductor is prepared as follows: Add 300 ml. of 2 per cent mercuric nitrate (or chloride) solution and 1 to 2 ml. of concentrated nitric acid to 300 g. of *pure* 20- to 30-mesh zinc in a beaker. Stir the mixture thoroughly for five to ten minutes, then decant the solution from the zinc, and wash two or three times by decantation. The amalgamated zinc should have a bright silvery luster. Fill the reductor tube with water, then add the zinc slowly until the column is completely packed. Wash with 500 ml. of distilled water, using gentle suction; leave the reductor full of water after the washing to prevent the formation of basic salts, which tend to clog the zinc column.

Procedure for reduction of ferric iron with the Jones reductor. The ferric sulfate solution to be reduced may have a volume of 100 to 150 ml.; it should be about 2 N in sulfuric acid and should contain not more than 0.25 g. of iron. Wash out the reductor first with 150 to 200 ml. of 1 : 20 sulfuric acid, added in 30 ml. portions; attach a clean flask to the reductor, and, using gentle suction, pass the cold ferric iron solution through the column at a rate not exceeding 75 ml. per minute. Do not allow the level of liquid in the reductor to fall below the top of the zinc column during the reduction.

---

[1] C. Jones, Trans. Am. Inst. Mining Engrs. *17*, 411 (1888–1889); for a discussion of significant factors in efficiency of amalgamated zinc, see H. W. Stone and D. N Hume, Ind. Eng. Chem., Anal. Ed. *11*, 598 (1939).

When all the iron solution has been drawn into the reductor, wash out the container with three 25 ml. portions of 1 : 20 sulfuric acid, add the washings to the reductor, and draw each portion through before adding the next. Finally, wash out the reductor with three 25 to 35 ml. portions of water. The final washing with water is necessary to remove all acid and prevent excessive consumption of zinc. A test for complete reduction of the iron may be made by adding one drop of the reduced solution to a drop of potassium thiocyanate on a spot plate. No red color will be obtained if reduction is complete.

Disconnect the flask from the reductor, wash off the end of the delivery tube, add 25 ml. of Zimmermann-Reinhardt solution, and titrate immediately with 0.1 *N* potassium permanganate solution in exactly the same manner as described on page 602.

Run a blank determination by passing 200 ml. of 1 : 20 sulfuric acid through the reductor in exactly the same manner as described above, and titrate the solution with 0.1 *N* permanganate. Subtract the blank thus found from the volume of permanganate used in the actual determination. If the zinc is pure, the correction should be less than 0.05 ml. of 0.1 *N* permanganate. It is best to run the blank before passing the solution to be reduced through the reductor to be sure that the reductor is in good working order.

NOTES:

1. As regards acidity, solutions 0.5 to 5 *N* in hydrochloric or sulfuric acid can be used. Sulfuric acid is preferable to hydrochloric acid because the latter may interfere in the subsequent titration (p. 499).

2. Solutions containing compounds of copper, tin, arsenic, antimony, and other reducible metals must never be used. If these substances are present they must be removed before the reduction. Platinum, derived in small amounts from platinum vessels, is quickly reduced to metal in the upper part of the zinc column and hence does not interfere.

3. Nitric acid or nitrates must not be present in the solutions to be reduced, since a more or less complete reduction to hydroxylamine and other compounds takes place. If nitric acid is present, evaporate the solution to dryness, add 3 ml. of water and 2 ml. of concentrated sulfuric acid, and evaporate to fumes of sulfuric acid. Repeat the evaporation with sulfuric acid a second time to insure complete removal of the nitric acid, then dilute to 100 ml. with water, add 4 to 5 ml. of concentrated sulfuric acid, and proceed with the reduction.

4. Organic compounds, which may consume permanganate, must be absent. These may be destroyed by heating with concentrated nitric and sulfuric acids, finally evaporating several times with sulfuric acid to assure the expulsion of all nitric acid.

5. Other elements which are reduced to a definite stage in the reductor are molybdenum, chromium, titanium, and vanadium. Uranium is reduced mostly to the quadrivalent state but partly to the trivalent; since trivalent uranium is very unstable in air, the over-reduction may be easily corrected for by passing a current of air through the solution after reduction. In this way any trivalent uranium is quickly oxidized to the quadrivalent state, in which it is quite air-stable.[1]

The quadrivalent uranium may then be titrated with permanganate in the same manner as ferrous iron.

---

[1] G. E. F. Lundell and H. B. Knowles J. Am. Chem. Soc. *47*, 2637 (1925).

6. With the exception of iron and uranium (UO^{++}), the reduced solutions are unstable in air, and hence they must be protected from air oxidation after reduction. This is easily done by arranging the receiver so that the end of the outlet tube of the reductor dips below a solution of ferric sulfate or ferric alum contained in the receiver. When the reduced solution flows into the ferric solution, an equivalent amount of ferric iron is reduced to the ferrous state and the ferrous iron thus formed may be titrated with a suitable oxidizing agent.

Reduction with stannous chloride. In hot solution ferric ions are rapidly reduced by stannous ions (added in the form of stannous chloride). The excess of stannous tin can be destroyed by adding mercuric chloride, which is reduced to mercurous chloride. Mercurous chloride is not acted upon appreciably by the oxidizing agents used to titrate ferrous iron and may be left in the solution after the reduction. This method of reducing iron is very often used in the analysis of iron ores.

Great care must be taken not to add more than a very slight excess of stannous chloride in reducing the iron, or else metallic mercury may be formed on the addition of mercuric chloride:

$$Sn^{++} + HgCl_2 \rightarrow Sn^{++++} + Hg + 2\ Cl^-.$$

The formation of free mercury (indicated by a gray or black precipitate) ruins the determination, because the metal in a finely divided form is oxidized by permanganate (and dichromate). The reaction between stannous chloride and mercuric chloride is always allowed to take place in a cold solution, and the mercuric chloride is added as rapidly as possible. The presence of much mercurous chloride in the solution is objectionable, because it may be oxidized somewhat by potassium permanganate or ferric iron; this is another reason for limiting the excess of stannous chloride to the minimum quantity necessary. Detailed directions for the reduction of ferric iron with stannous chloride are given below under the determination of iron in an ore.

Determination of iron in an iron ore. The principal ores of iron are composed of oxides or hydrated oxides of iron:

Fe_2O_3 (hematite)
Fe_3O_4 (magnetite)
$Fe_2O_3 \cdot H_2O$ (goethite); $[Fe_2O_3 \cdot H_2O] \cdot x\ H_2O$ (limonite).

The carbonate, $FeCO_3$ (siderite), is a minor ore.

Ores consisting of the anhydrous oxides, Fe_2O_3 and Fe_3O_4, dissolve only slowly in acids, the others rather easily. Concentrated hydrochloric acid is the best acid to use in effecting solution. Sulfuric acid and oxidizing acids such as nitric acid are not suitable. The addition of stannous chloride greatly aids in the solution of hematite and magnetite ores. It is very important to employ a finely ground sample to hasten solution. A completely decomposed ore will give a residue of silica that is white or nearly so. If any dark material remains after the acid treatment, it is necessary to fuse the washed residue with sodium carbonate and treat the fusion product with hydrochloric acid to recover all the iron.

The minor constituents of iron ores include: silica, aluminum, calcium, magnesium, manganese, the alkalies, phosphorus, sulfur, titanium, vanadium, chromium, and other elements as well. Organic matter is sometimes present. Of these, it is necessary in a volumetric determination of iron to consider the possible effect of titanium, vanadium, chromium, and organic matter. Titanium does not interfere if the iron is reduced with stannous chloride but does do so if the reduction is effected by metals, e.g., the Jones reductor. The use of the latter is generally inadmissible in the analysis of iron ores because titanium is usually present, sometimes in quite large amounts. Vanadium is reduced by stannous chloride to vanadyl ion, and the latter is not oxidized by mercuric chloride and therefore remains to be oxidized by potassium permanganate. If the titration is made with potassium dichromate, using diphenylamine sulfonic acid as an internal indicator instead of potassium permanganate solution, there is no interference from vanadium at the proper acidity. Chromium is not often met with in appreciable quantities in iron ores; it is not reduced by stannous chloride and therefore does not interfere. Organic matter is easily destroyed by treating the acid solution with potassium chlorate or permanganate before adding stannous chloride or by igniting the sample before dissolving.

Procedure. Special solutions required:

Stannous chloride. — 150 g. of iron-free $SnCl_2 \cdot 2\ H_2O$ in 1 liter of 1 : 2 hydrochloric acid. This solution should be freshly prepared.

Mercuric chloride. — 5 per cent solution of $HgCl_2$ in water.

Zimmermann-Reinhardt solution. — Dissolve 70 g. of $MnSO_4 \cdot 4\ H_2O$ in 500 ml. of water, add with stirring 125 ml. of concentrated sulfuric acid and 125 ml. of 85 per cent phosphoric acid, and dilute to approximately 1 liter.

Transfer 0.3 to 0.35 g. of finely ground air-dried ore to a 250 ml. beaker;[1] add 10 ml. of concentrated hydrochloric acid and 3 ml. of stannous chloride solution, and heat on the steam bath until the iron has been dissolved as indicated by a *white* residue. If any dark particles remain, add a few drops of concentrated nitric acid and continue the digestion, adding more nitric acid a little at a time until the residue is entirely white or it is seen that nitric acid is without effect. If the addition of nitric acid was necessary, evaporate the liquid to dryness, and heat for a short time at 110° to insure the expulsion of the acids. Take up the residue in 10 ml. of 1 : 1 hydrochloric acid. The presence of any dark particles at this point calls for fusion of the residue with sodium carbonate.[1] Proceed as follows. Filter off the insoluble material, using a small filter paper, and wash the residue with dilute hydrochloric acid. Place the paper and its contents in a porcelain crucible,[2] burn off the paper, ignite the residue, and fuse it with 0.5 g. of sodium carbonate. Take up the melt in a small excess of hydrochloric acid and add the solution, with any suspended material, to the main iron solution.

---

[1] If it is known, or there is reason to suspect, that the ore contains organic matter, ignite it, after weighing, at low redness in an uncovered porcelain crucible and then transfer quantitatively to a beaker.

Dilute or concentrate the iron solution, as the case requires, to 15 or 20 ml. Not much more than the equivalent of 5 ml. of concentrated hydrochloric acid should be present. Add dropwise a 2 or 3 per cent solution of potassium permanganate until a yellow color is produced. Heat the solution nearly to boiling, and add the stannous chloride solution carefully from a pipet drop by drop with stirring, until the yellow color of the ferric ions has disappeared, and then *1 or 2* drops more. Cool the solution to room temperature (not over 25°), and add 10 ml. of mercuric chloride solution all at once. The precipitate obtained should be white and silky, and *small in amount;*[3] if it is gray, indicating the presence of finely divided elemental mercury, the solution must be rejected. Wait two or three minutes, not longer, and then pour the solution into a 600 ml. beaker or a large casserole containing 25 ml. of Zimmermann-Reinhardt solution and 300 ml. of water. Titrate slowly with 0.1 N potassium permanganate solution, not adding the standard solution more rapidly than the drops can be counted. The end point is indicated by a faint permanent pink coloration. Report the percentage of iron in the sample.

In the most accurate work a blank determination should be carried through all the steps of the procedure.

Further titrations with permanganate.

Nitrite. Nitrite does not react with permanganate in neutral or alkaline medium; in warm acid medium it is oxidized quantitatively to nitrate:

$$5\,NO_2^- + 2\,MnO_4^- + 6\,H^+ \rightarrow 5\,NO_3^- + 2\,Mn^{++} + 3\,H_2O.$$

---

[1] In the most accurate analyses the residue should be fused with sodium carbonate even if it does not appear to contain any iron.

[2] Platinum crucibles are not to be used in the sodium carbonate fusion in this case because the small amount of platinum thus introduced would interfere subsequently in the reduction of the ferric iron with stannous chloride.

[3] If no precipitate appears, sufficient stannous chloride was not added in the reduction of the iron, and the sample must be discarded.

If an acidified nitrite solution is slowly titrated with permanganate, poor results are obtained because nitrous acid is volatile and unstable; and in addition an air oxidation takes place giving rise to the formation of nitrate. It is better therefore to add the nitrite solution from a buret to a measured volume of acidified standard permanganate solution until the latter is decolorized. This is the classical procedure of Lunge;[1] it is not very accurate since nitrite does not react instantaneously with the permanganate and losses may occur by volatilization or decomposition of the nitrous acid before it has reacted with the oxidizing agent.

It is better to use the second procedure described below, in which the nitrite solution is mixed with an excess of permanganate, the mixture acidified, and the excess of permanganate titrated back iodometrically or according to any of the other methods mentioned for the titration of permanganate (see p. 582).

Procedure 1 (*of Lunge*). Prepare an approximately 0.1 N solution of the nitrite. Pipet 25 ml. of 0.1 N potassium permanganate solution into a 500 ml. flask, add 25 ml. of 1 : 5 sulfuric acid and 250 ml. of water, heat to 40°, and titrate with the nitrite solution. Add the nitrite very slowly with constant stirring towards the end of the titration when the solution has a pale violet color. The accuracy of the titration is usually about 0.5 to 1 per cent.

Procedure 2. Pipet 50 ml. of 0.1 N potassium permanganate solution into a glass-stoppered flask, add 5 ml. of 1 : 5 sulfuric acid and 25 ml. of approximately 0.1 N nitrite solution. Stopper the flask, shake frequently, and after fifteen minutes' standing add 2 g. of potassium iodide and titrate with standard thiosulfate solution (p. 625).

NOTES:

1. Use is made of the oxidimetric nitrite determination in the determination of potassium. This cation is precipitated with a solution of sodium cobaltinitrite in the form of a yellow precipitate which has the approximate composition $K_2NaCo(NO_2)_6 \cdot H_2O$. After washing and drying, the precipitate can be weighed in the anhydrous form or can be treated with an excess of acidified permanganate solution and the excess back-titrated. The nitrite is oxidized to nitrate, whereas the trivalent cobalt is reduced to the divalent state. Hence 1 mole of the cobaltinitrite precipitate requires 11 equivalents of permanganate. Unfortunately the method is not precise; the composition of the precipitate varies with the composition of the reagent, the speed and mode of precipitation, and the presence of other ions in the solution. The ratio of K to Na in the precipitate is not exactly 2 : 1; if the solution contains sodium salts the ratio becomes much smaller. If alkaline earth metals are present, they will replace part of the potassium and sodium in the precipitate. The method is therefore highly empirical.

2. Better results are obtained in the volumetric determination of cobalt by precipitation as potassium cobaltinitrite, $2\ K_3Co(NO_2)_6 \cdot 3\ H_2O$. An acetic acid solution of the cobalt salt is treated with a large excess of potassium nitrite. The precipitate is filtered off, after not less than twelve hours of standing, washed with 2 per cent ammonium nitrate solution, dissolved at

---

[1] G. Lunge, Z. angew. Chem. *4*, 629 (1891); Chem. Ztg. *26*, 501 (1904).

50° in an excess of an acidified potassium permanganate solution, and the excess of the latter is back-titrated iodometrically. One mole of cobalt corresponds to 11 equivalents of permanganate. The method has the advantage that nickel and most other metals do not interfere.

Hydrogen peroxide. In acid solution, hydrogen peroxide reduces permanganate, oxygen being formed:

$$5\,H_2O_2 + 2\,MnO_4^- + 6\,H^+ \rightarrow 5\,O_2 + 2\,Mn^{++} + 8\,H_2O.$$

The first drops of permanganate are decolorized slowly, but afterwards the reaction runs smoothly to the end point (see p. 593). If a little manganous salt is added at the beginning, the first few drops of permanganate are reduced at once.

Procedure. Weigh out 3 g. of commercial hydrogen peroxide solution (about 3 per cent H_2O_2). Transfer the sample to a 250 ml. volumetric flask, and dilute with water to the mark. Pipet out 25 ml., add 10 ml. of 1 : 5 sulfuric acid, and titrate with 0.1 *N* permanganate solution.

NOTES:

1. Hydrogen peroxide solutions are not stable over a long period of time. Small amounts of organic substances, such as acetanilid, urea, and uric acid, are often added to commercial products to render them more stable. Since these organic substances, with the exception of urea, consume permanganate, the above method does not give accurate results in their presence. Under such circumstances it is better to resort to the iodometric method (p. 630).

2. Alkali and alkaline earth peroxides, percarbonates, and perborates can be titrated in the same way as hydrogen peroxide, if they are dissolved in dilute acid.

Determination of available oxygen in higher oxides of manganese and lead.

The higher oxides of lead, such as lead dioxide, PbO_2, minium, Pb_3O_4, and the higher manganese oxides (e.g., pyrolusite, MnO_2) may be determined by reducing with an excess of standard arsenious oxide or oxalic acid solution, and after solution back-titrating the excess of the latter with standard permanganate solution or any other suitable oxidizing agent. The use of arsenious oxide is to be preferred to that of oxalic acid, because the latter slowly decomposes at higher temperatures to carbon dioxide and carbon monoxide (p. 593). This decomposition is catalyzed by manganous salts, which are formed during the reduction of the pyrolusite. In technical laboratories an acid ferrous sulfate solution is often used as the reducing agent. Good results are obtained if the hot solution is protected from the air during the reaction (see p. 589).

$$2\,MnO_2 + As_2O_3 + 4\,H^+ \rightarrow 2\,Mn^{++} + As_2O_5 + 2\,H_2O$$
$$MnO_2 + H_2C_2O_4 + 2\,H^+ \rightarrow Mn^{++} + 2\,H_2O + 2\,CO_2$$
$$MnO_2 + 2\,Fe^{++} + 4\,H^+ \rightarrow Mn^{++} + 2\,Fe^{+++} + 2\,H_2O.$$

Procedure for determination of available oxygen in pyrolusite. Boil 0.2 g. of the very finely powdered sample of pyrolusite in an Erlenmeyer flask with 50 ml. of 0.1 N arsenious oxide solution (p. 622) and 10 ml. of concentrated sulfuric acid to complete decomposition as indicated by the disappearance of brown or black particles. Cool the solution, add 100 ml. of water, 5 ml. of hydrochloric acid, and 1 drop of 0.002 M potassium iodate solution (catalyst, see p. 594), and titrate with permanganate. Standardize the arsenious oxide solution by running a blank, following the steps of the procedure. In the analysis of PbO_2 or Pb_3O_4, 0.5 g. samples are taken, and 10 ml. of concentrated hydrochloric acid are used instead of sulfuric acid. A condenser should be used during the heating to prevent volatilization of $AsCl_3$.

Determination of calcium after precipitation as calcium oxalate.

Metals which give slightly soluble oxalates may be determined permanganimetrically by dissolving the washed precipitate in hot dilute sulfuric acid and titrating with standard potassium permanganate solution. This method is very often used for the determination of calcium.

The precipitation of calcium as oxalate has already been considered (p. 347). It is only necessary here to call attention to the fact that if the precipitate is formed by adding ammonium oxalate to a neutral or ammoniacal solution of calcium, the calcium oxalate obtained is contaminated with basic oxalate or calcium hydroxide, and the results of the permanganate titration will be low, sometimes to the extent of 1 per cent. If the precipitation is made as described under the gravimetric determination of calcium by the addition of oxalate to a dilute hydrochloric acid solution of the element, followed by the neutralization of the acid with dilute ammonia, there is obtained a precipitate of nearly the theoretical composition. A small amount of coprecipitated ammonium oxalate and probably oxalic acid are present in precipitates so formed, so that the results are high by approximately 0.2 per cent, if the volume of wash water used is restricted to the smallest necessary amount, to avoid solubility losses.[1] The accuracy of the volumetric method compares favorably with that of the gravimetric, and the former is more rapid when many samples are to be analyzed.

Procedure. (For interfering substances, see p. 348.)

---

[1] H. Bassett, J. Chem. Soc. *1934*, 1273, recommends the use of saturated calcium oxalate solution for washing.

Weigh out duplicate samples containing 0.07 to 0.09 g. of calcium, and precipitate calcium oxalate as described on page 358. Allow the precipitate to stand for an hour, and then filter it off in a Gooch, glass, or porcelain filter crucible. Wash crucible and precipitate with small portions of cold water until the washings are chloride-free, avoiding the use of more water than is really necessary. Dissolve the precipitate by pouring 1 : 8 sulfuric acid[1] into the crucible, allowing the acid to remain in the crucible for a minute or two before drawing it into the suction flask.[2] Solution of the calcium oxalate is hastened by stirring it up in the liquid with a short stirring rod kept in the crucible. Continue drawing hot dilute sulfuric acid through the crucible until all of the precipitate is dissolved. Not more than 50 ml. should be required. Examine the filter crucible carefully at the end, to be sure that no precipitate remains undissolved. Dilute the solution with water until the sulfuric acid concentration is 1 to 1.5 *N*, heat to 80°, and titrate slowly with standard potassium permanganate to the first pink tinge (for correction for excess see p. 594).

PROBLEMS

1. A 0.2250 g. sample of a mixture consisting only of iron and ferric oxide (Fe_2O_3) was brought into solution, and the iron was reduced to the divalent state and titrated with potassium permanganate. If 37.50 ml. of 0.0991 *N* permanganate were required, calculate the percentages of Fe and Fe_2O_3 in the sample. *Ans.* 74.1 per cent Fe; 25.9 per cent Fe_2O_3.

2. 25.00 ml. of a solution containing cobalt and nickel were treated with an excess of potassium nitrite in the presence of acetic acid to precipitate cobalt. After washing, the precipitate was dissolved in 50 ml. of 0.0990 *N* permanganate. Then 20.00 ml. of 0.1010 *N* ferrous iron solution were added, and the excess ferrous iron was titrated with 0.0990 *N* potassium permanganate, 12.37 ml. of the latter being required. Calculate the weight of the cobalt in the solution. Give equations. *Ans.* 0.0222 g. Co.

3. Outline methods for the determination of ferrous, ferric, and total iron in a mixture of divalent and trivalent iron.

4. Manganous manganese is quantitatively oxidized by permanganate in hot neutral or weakly acid medium according to the equation:

$$3\,Mn^{++} + 2\,MnO_4^- + 2\,H_2O \rightarrow 5\,MnO_2 + 4\,H^+.$$

If zinc sulfate or a mixture of the latter with zinc oxide is added to prevent adsorption of manganous ions by the manganese dioxide, the end point is indicated by the appearance of a pink color in the supernatant liquid after the precipitate has settled.

---

[1] The sulfuric acid solution used should be tested for reducing substances with permanganate.

[2] It is convenient to receive the acid solution directly in a 250 ml. flask so that it will not be necessary to transfer the solution before the titration.

In such a titration it was found that 35.70 ml. of standard permanganate were required. The latter had been standardized against sodium oxalate according to the usual procedure and found to be 0.1000 *N*. What is the manganese content of the solution?

Ferric iron if present does not interfere since it is precipitated in the form of hydrous ferric oxide by the zinc oxide added. How could manganese be determined by the above method in a solution containing ferrous iron?

Ans. 0.0588 g. Mn.

5. A solution contains ferric chloride and hydrogen peroxide. Give procedures by which one can determine the peroxide and the ferric iron by titration with permanganate.

6. A solution contains ferrous sulfate and potassium bromide. How may the bromide (argentimetrically) and the ferrous iron be determined? (Bromide interferes with the titration of ferrous iron with permanganate.)

CHAPTER XXXVIII

TITRATIONS WITH POTASSIUM DICHROMATE AND CERIC SULFATE

POTASSIUM DICHROMATE

Use of potassium dichromate.

Potassium dichromate is obtained pure by twice recrystallizing a C. P. product from water, followed by drying of the pulverized crystals at 150° to 200° in an electric oven.

Solutions of potassium dichromate in water are stable indefinitely; even when acidified with dilute sulfuric, perchloric, or hydrochloric acids, there is no reduction on boiling. On boiling with more concentrated hydrochloric acid, however, a reduction takes place with the simultaneous evolution of chlorine. At room temperature, titrations can be made with dichromate in the presence of hydrochloric acid if the concentration of the acid is less than about 1 to 2 *N*. This fact is of great importance in the titration of ferrous iron, because hydrochloric acid interferes in this case when permanganate is used. Dichromate solutions are also less easily reduced by organic matter than is permanganate.

The best indicator for the detection of the end point is sodium diphenylamine sulfonate, although diphenylamine and diphenylbenzidine can also be used. The ferrous-phenanthroline complex is less suitable, as has already been mentioned (p. 495).

Preparation of 0.1000 *N* standard potassium dichromate solution.

Weigh out 4.903 g. of pure dry potassium dichromate, dissolve in water, and dilute to exactly 1 liter.

Titration of ferrous iron.

If ferrous iron is titrated in the presence of hydrochloric or sulfuric acid, any of the three diphenylamine compounds being used as indicator, the color change is not sharp and occurs too early, because the indicator is partially oxidized before the end point is reached (p. 497). However, a sharp color change is produced at the equivalence point if phosphoric acid is added to the solution. Phosphoric acid lowers the oxidation potential of the ferric-ferrous iron system by forming a complex with the ferric ions, which explains its beneficial effect when using the above indicators.

The indicator blanks are negligibly small in titrations with 0.1 *N* solutions.

Determination of iron in an iron ore.

Indicator solution: A 0.2 per cent solution of sodium diphenylamine sulfonate in water.

Procedure. Bring the sample into solution, and reduce the iron as described under the permanganate method (p. 600). After the reduction with stannous chloride and addition of mercuric chloride, add 200 ml. of water, 10 ml. of 1 : 5 sulfuric acid, 5 ml. of 85 per cent phosphoric acid, and 6 to 8 drops of indicator. Titrate slowly with 0.1 *N* standard dichromate solution, stirring constantly, until the pure green color changes toward a gray-green. Then add the dichromate very slowly, one drop at a time, until the first tinge of purple or violet-blue appears. Run a blank determination with the reagents and make the proper correction, if necessary. Calculate the percentage of iron.

NOTES:

The color change of the indicator is reversible. Therefore if the solution is accidentally over-titrated, the excess oxidizing agent can be back-titrated with a standard ferrous iron solution. The oxidized form of the indicator is slowly destroyed by an excess of oxidizing agent, and the back-titration should therefore be made quickly.

The reverse titration of dichromate with ferrous sulfate also gives good results; use is made of it in the determination of chromium in chromium steels.

Vanadic acid can be titrated in the same way as chromic acid:[1]

$$VO_4^{\equiv} + Fe^{++} + 6\,H^+ \rightarrow VO^{++} + Fe^{+++} + 3\,H_2O.$$

This titration finds application in steel analysis (p. 725).

Titration of uranium and its application to the volumetric determination of sodium.

It has already been mentioned (p. 498) that sexivalent uranium (uranyl) is reduced to a mixture of tri- and quadrivalent uranium in the Jones reductor. After aeration to oxidize trivalent uranium to the quadrivalent state, the solution may be titrated with potassium dichromate, using ferric iron as a catalyst[1] and either diphenylamine, diphenylbenzidine, or diphenylamine sulfonate as indicator.

---

[1] N. H. Furman, Ind. Eng. Chem. *17*, 314 (1925).

$$3\ UO^{++} + Cr_2O_7^{=} + 8\ H^+ \rightarrow 3\ UO_2^{++} + 2\ Cr^{+++} + 4\ H_2O.$$

Potassium permanganate or ceric sulfate may also be used for titrating reduced uranium solutions.[2]

The titration of uranium may be used for a volumetric sodium determination by precipitating the sodium as $NaZn(UO_2)_3(CH_3COO)_9 \cdot 6\ H_2O$, as in the gravimetric determination of sodium (p. 416). The precipitate is dissolved in dilute sulfuric acid, the solution is reduced in the Jones reductor, and the reduced solution is titrated with standard dichromate solution. Since the ratio of uranium to sodium in the precipitate is constant, the result of the uranium titration can be used to calculate the amount of sodium present. This volumetric method is of practical importance in the determination of very small quantities of sodium (less than 1 mg.) when the amount of precipitate is too small to allow accurate weighing.

Procedure.[3] Precipitate, filter, and wash the sodium uranyl zinc acetate from a suitable weight of sample, as described in the gravimetric procedure (p. 597). The weighed precipitate from the gravimetric procedure may be used.

Place the filter crucible containing the triple salt in a Gooch funnel attached to a 250 ml. suction flask. Pour 50 to 75 ml. of 2 *N* sulfuric acid slowly through the crucible in several small portions, using gentle suction; then wash out the crucible and funnel with water. Dilute the solution to 100 ml., if not already at this volume, and add sufficient 6 *N* sulfuric acid to make the total acid concentration approximately 2 *N*. Reduce the solution in a Jones reductor in the same manner as described under the determination of iron (p. 598). The reduced solution should have the dark olive-green color characteristic of trivalent uranium. Place a long glass tube in the solution, and bubble a rapid stream of air through the liquid for five to ten minutes;[4] this treatment will oxidize all trivalent uranium to the quadrivalent state, and the solution will assume the clear green color of quadrivalent uranium. Wash off the tube with a small amount of water from a wash bottle; add 15 ml. of 85 per cent phosphoric acid, 40 ml. of 2 per cent ferric chloride solution, and 6 to 8 drops of diphenylamine sulfonate indicator. Titrate immediately with standard 0.1 *N* dichromate in the same way as described under the titration of ferrous iron (p. 609).

---

[1] In the absence of iron the end point is not good, evidently because the reaction between uranous ions and dichromate is relatively slow. Ferric iron, however, reacts very quickly with uranous ions,

$$UO^{++} + 2\ Fe^{+++} + H_2O \rightarrow UO_2^{++} + 2\ Fe^{++} + 2\ H^+,$$

and thus catalyzes the reaction.

[2] For a review of the literature on the uranium titration see N. H. Furman and J. C. Schoonover, J. Am. Chem. Soc. *53*, 2561 (1931).

[3] I. M. Kolthoff and J. J. Lingane, J. Am. Chem. Soc. *55*, 1871 (1933).

[4] If compressed air or suction is not available, transfer the solution to a beaker, stir vigorously for five to ten minutes until the color is a clear green, and then proceed as above.

CERIC SULFATE

Use of ceric sulfate.

The advantages of ceric sulfate over potassium permanganate have already been mentioned (p. 583). Ceric sulfate may be used in most titrations in which permanganate is employed.

Sulfuric acid solutions of pure ceric sulfate are stable even at boiling temperatures. Hydrochloric acid solutions of the salt are unstable owing to reduction of the ceric to cerous cerium by the hydrochloric acid, with simultaneous liberation of chlorine:

$$2\,Ce^{++++} + 2\,Cl^- \rightarrow 2\,Ce^{+++} + Cl_2.$$

This reaction takes place quite rapidly at boiling temperature, and hence hydrochloric acid cannot be used in oxidations which necessitate boiling with an excess of ceric sulfate in acid solution. In such oxidations sulfuric acid must be used. However, direct titrations with ceric sulfate in hydrochloric acid medium may be successfully performed, even in hot solution. For example, oxalic acid may be titrated with ceric sulfate in hot hydrochloric acid solution, and hydrochloric acid solutions of ferrous iron may be accurately titrated at room temperature. In this respect, ceric sulfate distinguishes itself very favorably from permanganate.

It should be mentioned that the presence of hydrofluoric acid is very harmful in ceric sulfate titrations. Fluoride forms a stable complex with ceric ions and decolorizes the yellow solution; with much fluoride at low acidities a precipitate of ceric fluoride is formed. Cerous salts also form complexes with fluoride, but these are less stable than the ceric complexes. Consequently, fluoride decreases the oxidation potential of the ceric-cerous system very strongly. A dilute sulfuric acid solution of ceric sulfate in the presence of much fluoride does not oxidize iodide for this reason.

Since ceric phosphate is only slightly soluble, a precipitate is obtained in dilute sulfuric acid solutions containing phosphate; but the precipitate is soluble in stronger acid. Ceric sulfate is always used in acid solution, since ceric hydroxide is a weak base, insoluble in water, and precipitates from neutral or weakly acid solutions as a result of hydrolysis.

The ferrous-phenanthroline complex is an excellent indicator in many titrations with ceric sulfate; diphenylamine sulfonate may also be used in certain titrations, for example, that of ferrous iron. In titrations of colorless solutions with 0.1 *N* ceric sulfate, the end point can be detected by the yellow color of the reagent itself (ceric ions are yellow, cerous colorless) without the use of a special indicator; the detection of the end point in this way is more satisfactory in hot than in cold solutions because of an increase in the intensity of the yellow color of ceric ions with a rise in temperature. An appreciable blank correction must be applied when the reagent serves as its own indicator, and for this reason a special indicator should be used whenever possible.

Preparation of 0.1 *N* standard ceric ammonium sulfate.

Solutions of ceric sulfate are most conveniently prepared from ceric ammonium sulfate, a salt which is commercially available in a fairly pure state. The salt has the composition $Ce(SO_4)_2 \cdot 2\,(NH_4)_2SO_4 \cdot 2\,H_2O$. An approximately 0.1 *N* solution is prepared as follows. Slowly add 30 ml. of concentrated sulfuric acid to 500 ml. of water with constant stirring, then add 63 g. of ceric ammonium sulfate dihydrate, and stir until solution is complete. Cool to room temperature, filter the solution if turbid, and dilute to 1 liter.

The commercial salt often contains traces of phosphate, which give rise to a slow precipitation of a small amount of ceric phosphate on standing. The rate of precipitation of ceric phosphate from the strongly acid solution is very slow, so that no errors result if the solution is used soon after standardization. However, if the solution is to be kept for some time, it should be allowed to stand for two weeks or longer and then filtered and standardized. A solution prepared in this way is stable for a long time.

Solutions of ceric sulfate may be standardized against sodium oxalate in hot hydrochloric or sulfuric acid solution, but the end point must then be determined without a special indicator or by the potentiometric method, because the oxidation-reduction indicators available at present are all oxidized before the equivalence point is reached. For this reason the method cannot be recommended for highly accurate work on account of the appreciable blank correction that must be applied when the reagent serves as its own indicator. It is better, therefore, to standardize against arsenious oxide, pure electrolytic iron, or potassium ferrocyanide.

If arsenious oxide is used, it is necessary to add a trace of osmium tetroxide or, less preferably, iodine monochloride as catalyst because otherwise the reaction between arsenious oxide and ceric sulfate is extremely slow. When osmium tetroxide is used as catalyst, the reaction is rapid at room temperature, and an excellent color change is obtained at the equivalence point with the ferrous-phenanthroline complex as indicator. With iodine monochloride as catalyst the reaction is somewhat slower than with osmium tetroxide, but accurate results are obtained if the titration is finished at 50° in the presence of sufficient hydrochloric acid.[1] It should be mentioned that when osmium is used as catalyst, the titration must be made in dilute sulfuric acid because hydrochloric acid interferes seriously.

Standardization against arsenious oxide.[2]

Weigh out 0.15 to 0.22 g. of pure dry arsenious oxide into a 250 ml. Erlenmeyer flask, and add 15 ml. of 2 *N* sodium hydroxide; warm gently to hasten solution. When the sample has completely dissolved, cool to room temperature, and add 25 ml. of 1 : 5 sulfuric acid. Dilute to 100 ml.; add 3 drops of 0.01 *M* osmium tetroxide (0.25 g. of OsO_4 in 100 ml. of 0.1 *N* sulfuric acid) as catalyst and 1 drop of ferrous-phenanthroline indicator. Titrate with 0.1 *N* ceric ammonium sulfate solution until the reddish-orange color changes sharply to colorless or very pale blue.

NOTE:

If iodine monochloride is used as catalyst, proceed as follows. Prepare the iodine monochloride solution by dissolving 0.1395 g. of potassium iodate and

---

[1] H. H. Willard and Ph. Young, J. Am. Chem. Soc. *55*, 3260 (1933).

[2] K. Gleu, Z. anal. Chem. *95*, 305 (1933).

0.0890 g. of potassium iodide in 125 ml. of water and adding all at once 125 ml. of concentrated hydrochloric acid. Cool to room temperature and adjust the solution as follows. Add 5 to 10 ml. of chloroform and titrate very carefully with either dilute potassium iodate or dilute potassium iodide, as the case may require, until the chloroform layer shows only a very faint iodine color after vigorous shaking.

Dissolve the sample of arsenious oxide as described above, and add 20 ml. of concentrated hydrochloric acid. Dilute to 100 ml.; add 2.5 ml. of the iodine monochloride solution and 1 drop of ferrous-phenanthroline indicator. Titrate with the ceric sulfate solution until the reddish-orange color begins to fade and returns only slowly after the addition of each drop of oxidizing agent. Heat the solution to 50° (use a thermometer), and continue the dropwise addition of ceric sulfate until the color is discharged and there is no return of the orange color of the indicator within one minute.

Determination of the ferrocyanide content of commercial potassium ferrocyanide.

Weigh out a 1.0 to 1.2 g. sample of commercial potassium ferrocyanide and dissolve in 80 ml. of water. Add 20 ml. of 1 : 5 sulfuric acid and 1 drop of ferrous-phenanthroline indicator. Titrate with 0.1 *N* ceric ammonium sulfate solution until the color changes sharply from orange to pure yellow.

Calculate and report the percentage of $K_4Fe(CN)_6$ in the sample.

NOTES:

1. Instead of using the ferrous-phenanthroline complex as indicator, two to three drops of a 2 per cent solution of ferric chloride may be added to the solution.[1] The greenish coloration due to ferric ferrocyanide disappears sharply at the equivalence point in consequence of the oxidation of ferro- to ferricyanide, and the color of the solution then changes to pure yellow.

2. The above method cannot be applied if the impure potassium ferrocyanide contains organic material, thiocyanate, or other substances oxidizable by ceric sulfate.

---

[1] N. H. Furman and O. M. Evans, J. Am. Chem. Soc. *51*, 1128 (1929).

CHAPTER XXXIX

IODIMETRY AND IODOMETRY

Iodimetric and iodometric methods.

The reaction:

$$I_2 + 2\,e \rightleftarrows 2\,I^-$$

is reversible. Substances with an oxidation potential much lower than that of the iodine-iodide system are oxidized by iodine and can be titrated with a standard iodine solution (*iodimetry*).

Examples:

$$SO_3^{=} + I_2 + H_2O \rightarrow SO_4^{=} + 2\,I^- + 2\,H^+$$
$$S^{=} + I_2 \rightarrow S + 2\,I^-$$
$$2\,S_2O_3^{=} + I_2 \rightarrow S_4O_6^{=} + 2\,I^-$$
$$Sn^{++} + I_2 \rightarrow Sn^{++++} + 2\,I^-.$$

On the other hand, iodide exerts a reducing action upon strongly oxidizing systems, with the formation of an equivalent amount of iodine. The liberated iodine is titrated with standard thiosulfate solution (*iodometry*).

Examples:

$$2\,Ce^{++++} + 2\,I^- \rightarrow 2\,Ce^{+++} + I_2$$
$$BrO_3^- + 6\,I^- + 6\,H^+ \rightarrow Br^- + 3\,I_2 + 3\,H_2O$$
$$2\,MnO_4^- + 10\,I^- + 16\,H^+ \rightarrow 2\,Mn^{++} + 5\,I_2 + 8\,H_2O.$$

The oxidation potential of the iodine-iodide system is virtually independent of the pH of the solution as long as the latter is less than about 8; at higher alkalinities iodine reacts with hydroxyl ions to form hypoiodite and iodide. The hypoiodite is extremely unstable and is very rapidly transformed into iodate:

$$I_2 + 2\,OH^- \rightarrow IO^- + I^- + H_2O$$
$$3\,IO^- \rightarrow 2\,I^- + IO_3^-.$$

Substances which do not possess oxidizing or reducing properties hardly affect the oxidation potential of the iodine-iodide system. This is not true of many other oxidation-reduction systems. On page 485 it was mentioned that the oxidation potential of substances which upon reduction give up oxygen with the formation of water increases very much with increasing hydrogen-ion concentration of the solution. This, for example, is the case with systems involving permanganate, dichromate, vanadate, bromate, etc. A neutral chromate solution, for example, does not react with iodide, whereas in acid medium chromate is quantitatively reduced to trivalent chromium. By the proper adjustment of the pH it is sometimes possible to titrate the reduced form of a substance with iodine, and its oxidized form with thiosulfate after addition of iodide. This, for example, is the case with the arsenious oxide-arsenate system.

$$As_2O_3 + 2\,I_2 + 5\,H_2O \rightleftarrows 2\,H_3AsO_4 + 4\,I^- + 4\,H^+.$$

This reaction is completely reversible; at pH values between 9 and about 4, arsenious oxide can be titrated with iodine solution. In strongly acid medium, on the other hand, arsenate is reduced to arsenious oxide, the reaction then going from right to left as written above. Upon titration with thiosulfate the iodine is removed, and the displacement of the equilibrium from right to left is thus aided.

The oxidation potential of various systems can be changed by the addition of a substance which forms a complex, a slightly dissociated, or a slightly soluble compound with one of the two components (or with both, but then of different stability or solubility). The reaction between ferric iron and iodide

$$2\,Fe^{+++} + 2\,I^- \rightarrow 2\,Fe^{++} + I_2$$

can be made the basis of an iodometric iron titration. However, if fluoride or phosphoric acid is added, the ferric iron is transformed into a complex which no longer reacts with iodide. Pyrophosphate has a similar effect. Use is often made of this behavior in preventing the reduction of ferric iron by iodide in the iodometric determination of other substances.

The oxidation potential of the cupric-cuprous system is lower than that of iodine-iodide. In spite of this the reaction:

$$2\,Cu^{++} + 4\,I^- \rightleftarrows 2\,CuI + I_2$$

runs quantitatively to the right. The cuprous ions formed disappear in the form of the extremely slightly soluble cuprous iodide, and consequently the oxidation potential of the copper system is raised. If, on the other hand, the cupric ions are transformed into a complex as, for example, by the addition of tartrate or citrate, the above reaction runs quantitatively from right to left.

From the above it is evident that the conditions prevailing in a system being titrated may have a great effect upon the equilibrium conditions. If, in an iodometric titration, equilibrium is such that a measurable amount of the substance is still present in the higher state of oxidation, the complete reduction may be aided by: increase of the hydrogen-ion concentration, increase of the iodide concentration, slow titration with thiosulfate by which the iodine is removed, addition of a suitable catalyst, or removal of the iodine by extraction with organic solvents (chloroform or carbon tetrachloride) or by distillation. The distillation method is applied with slight modifications to the determination of available oxygen in the higher oxides of manganese and lead. In the evaluation of pyrolusite the sample may be boiled with hydrochloric or hydrobromic acid and the liberated chlorine or bromine absorbed in potassium iodide solution:

$$MnO_2 + 4\,H^+ + 4\,Cl^- \rightarrow Mn^{++} + 2\,H_2O + Cl_2 + 2\,Cl^-$$
$$Cl_2 + 2\,I^- \rightarrow 2\,Cl^- + I_2.$$

It is not advisable to boil the sample with an acid iodide solution, since the latter is a much stronger reducing agent than chloride and will react with ferric iron, which is a common impurity in pyrolusite:

$$2\,Fe^{+++} + 2\,I^- \rightleftarrows 2\,Fe^{++} + I_2.$$

An important application of iodometric methods is made in the determination of the acid content of solutions. The reaction

$$IO_3^- + 5\,I^- + 6\,H^+ \rightarrow 3\,I_2 + 3\,H_2O$$

proceeds very rapidly and is quantitative. (If an excess of a neutral solution of potassium iodate and iodide is added to a dilute solution of hydrochloric acid or any other strong acid, the hydrogen ions yield an equivalent amount of iodine, which can be titrated with thiosulfate. This method is especially advantageous in the titration of very dilute solutions of strong acids, because a very sharp color change is obtained at the end point.

The iodometric titration of weak acids is not so simple. Upon the removal of the hydrogen ions by reaction with iodate and iodide, a buffer system of the weak acid and ~~its~~ salt is formed. At the resulting low hydrogen-ion concentration, the rate of the reaction between iodate, iodide, and hydrogen ions becomes very small. In such a case good results are obtained by adding an excess of standard thiosulfate after the addition of the iodate-iodide solution. The iodine formed in the reaction is thus removed, and the reaction velocity is thereby greatly increased. The excess of thiosulfate is finally back-titrated with a standard iodine solution.

Sources of error in iodimetry and iodometry.

Two important sources of error in iodimetric and iodometric titrations are the air oxidation of an acid iodide solution and the loss of iodine by volatilization.

Iodide in acid medium is slowly oxidized by oxygen:

$$4\,I^- + 4\,H^+ + O_2 \rightarrow 2\,I_2 + 2\,H_2O.$$

This reaction is extremely slow in neutral medium, but the velocity increases with increasing hydrogen-ion concentration and is greatly accelerated by direct sunlight, by the reaction between iodide and the substance to be reduced (an induced reaction, very pronounced in the iodometric vanadate titration in strongly acid medium), and by the presence of certain substances which exert a catalytic effect. Cuprous ion, for example, has an appreciable effect, as it is easily oxidized by air; the cupric copper thus formed reacts in turn with more iodide, etc. Nitrite and nitric oxide (NO), even if present only in the smallest traces, interfere markedly. Nitrite in acid medium reacts with iodide according to the reaction

$$2\,NO_2^- + 2\,I^- + 4\,H^+ \rightarrow 2\,NO + I_2 + 2\,H_2O.$$

Nitric oxide forms higher oxides of nitrogen by reaction with the oxygen of the air, and these oxides then react with iodide to form more iodine and nitric oxide, the cycle repeating itself indefinitely. If a trace of nitric oxide is present in the solution titrated, no permanent end point is found in the titration with thiosulfate; the starch-iodine color returns very quickly after the removal of the iodine.

In the iodometric titration of oxidizing agents in acid medium with an excess of iodide, the solution must not be allowed to stand any longer than is necessary before the titration of the iodine is made. If an appreciable period is required for the reaction to go to completion, the air in the vessel should be replaced by carbon dioxide. This can often be done in the following simple way: Acid is added to the solution to be titrated in an iodine flask; the air is then removed by successive additions of three or four portions of a few hundred milligrams of sodium bicarbonate. The potassium iodide is added in solid form and the flask stoppered immediately thereafter.

The other source of error lies in the comparative ease with which iodine is volatilized from its solutions. This volatility is materially decreased by the presence of a large excess of iodide, which reacts with iodine to form tri-iodide ions:[1]

$$I^- + I_2 \rightleftarrows I_3^-.$$

The excess of iodide displaces the equilibrium from left to right. Iodine solutions should never be exposed for any length of time to the atmosphere. In titrations at room temperature ($< 25°$) losses are negligibly small if the solution contains at least 4 per cent of potassium iodide.

Detection of the end point. Starch as indicator.

Iodine in aqueous iodide solutions has an intense yellow to brown color, and its presence is thus made evident even at high dilutions. A drop of 0.1 *N* iodine solution imparts a pale yellow color to 100 ml. of water. In otherwise colorless solutions iodine can serve as its own indicator. A more pronounced color change at the end point is obtained if starch is used as an indicator. Starch reacts with iodine in the *presence of iodide* to form an intensely blue-colored adsorption complex, visible even at very low iodine concentration. One hundred milliliters of water to which 50 to 100 mg. potassium iodide and a few ml. of 0.2 per cent starch solution have been added should become distinctly blue (not violet) upon the addition of one drop of 0.1 *N* iodine solution. The sensitivity of the starch reaction corresponds to an iodine concentration of 1 to 2×10^{-5} *N* at room temperature in the presence of a small amount of iodide (0.001 *N* or more); in the absence of iodide the reaction is less sensitive.

The sensitivity of the reaction decreases with increasing temperature of the solution. At 50° it is about ten times less sensitive than at 25°. Ethyl and methyl alcohols materially decrease the sensitivity of the reaction. In solutions containing more than 50 per cent of alcohol the blue color does not appear at all. On the other hand, small amounts of alcohol (less than 5 per cent) have hardly any effect.

The starch solution should be fresh or else should be properly preserved. It often happens that an old starch solution does not impart a blue color to a dilute iodide-iodine solution, but a violet or reddish one. Such a solution should not be used, because the reddish-violet adsorption compound is only slowly decolorized by thiosulfate and no sharp end point is obtained. A stable starch solution can be obtained by the following procedure.

---

[1] Standard iodine solutions are always prepared by dissolving iodine in potassium iodide solutions. Pure water dissolves very little iodine.

Preparation of starch solution.

Triturate 2 g. of soluble starch and 10 mg. of mercuric iodide (preservative) with a little water, and add the suspension slowly to 1 liter of boiling water. Continue boiling until the solution is clear; cool, and transfer to a glass-stoppered bottle.

Use 5 ml. of this starch solution for each 100 ml. of solution to be titrated. In the titration of iodine, starch should not be added until just before the end point is reached, since the fading of the color of the iodine is a good indication of the approach of the end point.

The indicator blank is negligibly small in iodimetric or iodometric titrations of 0.1 *N* solutions. With more dilute solutions it must be determined in a liquid having about the same composition that the solution titrated has at the end point.

Organic liquids for the detection of the end point.

The limit of visibility of the reddish-violet color of iodine in carbon tetrachloride and chloroform exceeds that of the iodine-starch compound. On shaking 50 ml. of 4×10^{-5} *N* iodine solution with 10 ml. of chloroform or carbon tetrachloride, the lower layer of organic liquid becomes distinctly violet. The use of these organic liquids for the detection of the end point offers advantages in the titration of extremely dilute solutions, in cases in which the reaction between iodine and the substance to be titrated is relatively slow, and in titrations in extremely strongly acid medium (titrations with iodate according to Andrews; see p. 585). The titrations must be made in bottles or flasks with ground-glass stoppers; after each addition of reagent the vessel must be well shaken, and some time must be allowed for the separation of the liquid into two layers.

The reactions between thiosulfate and iodine and arsenious oxide and iodine.

The most important reactions applied in iodometric titrations are those between sodium thiosulfate and iodine and between arsenious oxide and iodine.

Thiosulfate is oxidized to tetrathionate by iodine:

$$2\,S_2O_3^{=} + I_2 \rightarrow S_4O_6^{=} + 2\,I^-. \qquad (1)$$

Strong oxidizing agents, such as bromine and hypochlorite, oxidize thiosulfate quantitatively to sulfate. Other oxidizing agents, such as potassium permanganate, potassium dichromate, and ceric sulfate, give an incomplete oxidation to sulfate. For this reason an excess of iodide is always added in the determination of these oxidizing substances before titration with thiosulfate. Hypoiodite oxidizes thiosulfate to sulfate; a weakly alkaline iodine solution (for example, in sodium carbonate) gives a partial oxidation to tetrathionate and a partial oxidation to sulfate:

$$S_2O_3^{=} + 4\,I_2 + 10\,OH^- \rightarrow 2\,SO_4^{=} + 8\,I^- + 5\,H_2O. \qquad (2)$$

According to the normal reaction (oxidation to tetrathionate), 1 mole of thiosulfate corresponds to 1 *equivalent* of iodine ($\frac{1}{2}\,I_2$), whereas in the oxidation to sulfate 1 mole of thiosulfate consumes 8 equivalents of iodine. Therefore one will find less thiosulfate required for the titration of iodine in weakly alkaline medium than in neutral or acid medium (equation 1). More of the thiosulfate will be oxidized to sulfate (equation 2) the higher the hydroxyl-ion concentration. The iodine and iodide concentrations, the temperature, and the presence of foreign substances also affect the extent to which reaction (2) takes place.

In certain cases it is necessary to neutralize an acid iodine solution before titration with thiosulfate. This neutralization should not be made with an excess of sodium bicarbonate, because erroneous results (equation 2) will then be obtained. Thus in the titration of 25 ml. of 0.1 *N* iodine solution in the presence of 0.5 g. of sodium bicarbonate, 24.00 ml. of 0.1 *N* sodium thiosulfate were used, whereas with 2 g. of sodium bicarbonate only 22.5 ml. of 0.1 *N* thiosulfate were required to reach the end point. Neutralization with an excess of ammonium carbonate, disodium phosphate, or borax may cause errors as well. In the titration of 0.1 *N* iodine solutions the pH should be less than 7.6; of 0.01 *N* solution, less than 6.5; and of 0.001 *N* solutions, less than 5. Under these conditions the reaction between iodine and thiosulfate takes place quantitatively according to equation (1).

If acid iodine solutions must be neutralized before titration, a buffer solution (see p. 43) of the proper pH should be used. At the end of the titration the approximate value of the pH should be determined in order to be sure that the alkalinity was not too high during the titration. Ordinarily iodine solutions can be titrated in quite strongly acid medium if care is taken to stir or shake well. If it is necessary to make the titration of iodine in a weakly alkaline medium, standard arsenious oxide solution should be used instead of sodium thiosulfate for the purpose. In such a case an acid solution can be neutralized with an excess of sodium or potassium bicarbonate. However, since iodine vapor may be carried along with the escaping carbon dioxide, it is better to use instead a sufficient amount of borax or disodium phosphate.

At a pH of 8 the reaction between arsenious oxide and iodine is represented by the equation:

$$As_2O_3 + 2\,I_2 + 5\,H_2O \rightleftarrows 2\,HAsO_4^{=} + 4\,I^- + 8\,H^+.$$

This reaction is reversible, and it is seen that the hydrogen-ion concentration plays an important rôle in deciding the state of equilibrium. With a change in pH the following equilibria must be considered as well:

$$HAsO_4^{=} + H^+ \rightleftarrows H_2AsO_4^-$$
$$H_2AsO_4^- + H^+ \rightleftarrows H_3AsO_4.$$

Washburn[1] and Roebuck[2] found that the equilibrium constant at room temperature is:

$$K = \frac{[H_3AsO_4][H^+]^2[I^-]^2}{[H_3AsO_3][I_2]} = 5.5 \times 10^{-2}.$$

In the titration of arsenious oxide with iodine, the pH of the solution may have any value between 4 and 9. Results accurate to 0.1 per cent are obtained in the pH region between 5 and 9. At pH values less than 5 the reaction becomes rather slow, and the end point is reached only very gradually.

In the reverse titration — iodine with arsenious oxide — the pH should not exceed 9; at higher pH values some iodine reacts with the hydroxyl ions and escapes titration by formation of iodate. Trivalent antimony can be titrated in the same way as trivalent arsenic. To prevent the precipitation of basic antimony salts, the antimony is kept in solution as a complex by the addition of tartrate in the form of potassium sodium tartrate (Rochelle salt).

Preparation of standard solutions.

0.1 N sodium thiosulfate solution. Dissolve in 1 liter of freshly boiled, cooled water 25 g. of $Na_2S_2O_3 \cdot 5\,H_2O$, and add 0.1 g. of sodium carbonate to the solution. Allow the solution to stand for a day before standardizing.

It is not possible to prepare sodium thiosulfate solutions of definite strength by weighing out the pure salt *as purchased*, because sodium thiosulfate pentahydrate effloresces very easily and such a product therefore is not likely to contain the proper amount of water. If desired, sodium thiosulfate can be recrystallized and dried in a hygrostat (p. 131) over a saturated solution of calcium chloride hexahydrate, and the pentahydrate thus obtained can be weighed out accurately to give a solution of definite strength. However, sodium thiosulfate solutions prepared with the greatest care may change in titer slowly with the lapse of time (p. 590), and it is therefore best to standardize the solution at the time it is used. Thiosulfate solutions from which sulfur has separated should be discarded.

---

[1] E. W. Washburn, J. Am. Chem. Soc. *30*, 31 (1908); *35*, 681 (1913).

[2] J. R. Roebuck, J. Phys. Chem. *6*, 365 (1902); *9*, 727 (1905).

0.1 N iodine solution. Place 12.7 g. of reagent quality iodine (weighed on a trip scale) in a 250 ml. beaker; add 40 g. of iodate-free potassium iodide [1] and 25 ml. of water. Stir at intervals to hasten solution of the iodine, and when all has dissolved dilute to approximately 1 liter. Keep the solution in a *glass-stoppered* bottle, and store in a cool place. Protect the solution from the light as much as possible, and keep the stock bottle well stoppered.

It is possible to prepare standard iodine solutions by weighing out specially purified (resublimed) dry iodine, dissolving in potassium iodide solution, and diluting to a definite volume.

Purification of iodine. Commercial iodine is contaminated by chlorine, bromine, and water. For the purification 10 to 12 g. are triturated with 1 g. of potassium iodide and 2 g. of ignited lime to bind the water. This mixture is placed in a dry beaker, which is covered with a round-bottom flask containing cold water. The beaker is carefully heated over a very small flame and the iodine sublimed against the cold flask. The coarse crystals are collected, ground in an agate mortar, and dried in a calcium chloride desiccator with an ungreased cover.

Preparation of 0.1 N iodine by exact weighing of pure iodine. Place approximately 20 g. of potassium iodide in a large weighing bottle and dissolve in 5 ml. of water. Allow to stand until the bottle and its contents have come to room temperature; then stopper the bottle and weigh to 0.1 mg. Without splashing, introduce 6 to 6.5 g. of dry resublimed iodine (previously weighed on a rough balance), stopper, and again weigh to 0.1 mg. Transfer the solution quantitatively to a 500 ml. flask without undue delay and make up to the mark with water. Pour the well-mixed solution into a *glass-stoppered*, preferably brown, bottle and store in a cool dark place.

When the solution is taken from the bottle, the latter is opened for as short a time as possible to avoid possible loss of iodine by volatilization. Iodine solutions should not be titrated in beakers but in Erlenmeyer flasks.

Standard 0.1 N arsenious oxide solution. Pure arsenious oxide can be obtained from the Bureau of Standards [2] and also from various manufacturers.

---

[1] Test potassium iodide for iodate as follows: Dissolve 1 g. in 25 ml. of water; add 2 ml. of starch solution and 1 ml. of 6 *N* sulfuric acid. There should be no immediate appearance of a blue color.

[2] Prepared according to directions of R. M. Chapin, J. Am. Chem. Soc. *41*, 351 (1919).

The substance may be purified by recrystallization from hot 20 per cent hydrochloric acid. The crystal powder thus obtained is dried in a desiccator over sulfuric acid. For highly accurate work it is further purified by sublimation.

Preparation of 0.1 N solution. Weigh out 2.4725 g. of pure dry arsenious oxide and dissolve in 20 ml. of 1 *N* sodium hydroxide solution. Add 1 *N* sulfuric or hydrochloric acid to the solution until the reaction is neutral or only slightly acid to litmus paper. Transfer the solution to a 500 ml. volumetric flask and make up to the mark.

Standardization of 0.1 *N* thiosulfate solution.

Various standard substances are available. Potassium iodate, potassium bromate, and potassium dichromate are the most useful. Electrolytic copper, iodine, oxalic acid dihydrate, and potassium ferricyanide may also be used.[1]

Standardization against potassium iodate. Potassium iodate is obtained in a pure state by recrystallization from water and drying at 180°. Even with only a slight excess of hydrogen ions the following reaction rapidly goes to completion:

$$IO_3^- + 5\,I^- + 6\,H^+ \rightarrow 3\,I_2 + 3\,H_2O.$$

Procedure. Weigh out 0.14–0.15 g. of pure potassium iodate, dissolve in 25 ml. of water, and add 2 g. of potassium iodide (iodate-free) and 10 ml. of 1 *N* sulfuric or hydrochloric acid. Titrate with standard thiosulfate solution with constant stirring. Add a few ml. of starch solution when the color of the liquid has become a pale yellow, and continue the titration till the color changes from blue to colorless.

NOTES:

1. The only disadvantage involved in the use of potassium iodate is its small equivalent weight. If 0.150 g. is weighed out and the weighing error amounts to 0.2 mg., an error of 0.13 per cent is thus introduced. Therefore it is more accurate to prepare a standard solution of potassium iodate of exactly known normality (about 0.09 *N*); 50 ml. of this solution are pipetted out and treated according to the above procedure.

2. Potassium bromate may also be used for standardizing thiosulfate solutions. It is obtained in a pure state by recrystallizations from water and drying at 180°. With iodide and acid it reacts quantitatively according to the equation:

$$BrO_3^- + 6\,I^- + 6\,H^+ \rightarrow 3\,I_2 + Br^- + 3\,H_2O.$$

---

[1] For a more detailed discussion see I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis*, Vol. II.

This reaction, however, does not proceed as rapidly as that with iodate, and a higher acidity is required than in the case of the latter. At least 5 ml. of 4 *N* hydrochloric acid or 10 ml. of 4 *N* sulfuric acid should be added to 25 ml. of the bromate-iodide mixture if the titration is to be made immediately after adding the acid. Molybdate catalyzes the reaction very strongly, and it is advantageous to add a few drops of a 3 per cent ammonium molybdate solution in an iodometric bromate titration.

Standardization against potassium dichromate. In acid medium dichromate reacts with iodide according to the equation:

$$Cr_2O_7^{=} + 14\,H^+ + 6\,I^- \rightarrow 3\,I_2 + 2\,Cr^{+++} + 7\,H_2O.$$

The reaction does not take place instantaneously, but the speed increases very strongly with increasing hydrogen-ion concentration of the solution. For this reason the standardization should be made in a strongly acidified solution. However, the high acidity may introduce an error through the air oxidation of hydrogen iodide. If the standardization is carried out according to the procedure given below, the error resulting from the air oxidation is not greater than 0.05 per cent and therefore negligibly small for most cases.

In work of the highest accuracy it is best [1] to work at a lower acidity and to let the mixture stand in a closed flask from which all air has been displaced by carbon dioxide until the reaction is complete.

Procedure. Weigh out 0.2 g. of pure potassium dichromate (p. 608) and dissolve in 50 ml. of water. Add 2 g. of potassium iodide and 8 ml. of concentrated hydrochloric acid. Mix thoroughly and titrate with thiosulfate, swirling the liquid constantly until the brown color has changed to a yellowish-green. (What would happen if there were a local excess of thiosulfate in the acid solution, and how would this affect the results?) Add a few milliliters of starch solution and continue the titration until the color changes sharply from blue to light green.

NOTE:

The iodometric chromate titration finds application in the volumetric determination of barium and lead. Both of these ions yield very slightly soluble chromates with an excess of potassium chromate in neutral medium or in a medium buffered with a mixture of acetic acid and sodium acetate:

$$Ba^{++} + CrO_4^{=} \rightarrow BaCrO_4$$
$$Pb^{++} + CrO_4^{=} \rightarrow PbCrO_4.$$

The precipitate is washed with water, dissolved in dilute hydrochloric acid, and titrated according to the above directions. It is also possible to use an excess of standard chromate solution (standardized against thiosulfate) to precipitate the barium or lead, and back-titrate an aliquot part of the filtrate.

Standardization against potassium ferricyanide. Potassium ferricyanide is obtained in a pure state by recrystallization from water and drying at 100°. It has the advantage of a high equivalent weight. Ferricyanide reacts fairly slowly with iodide in acid medium, but the reaction is accelerated by the addition of zinc sulfate:

$$2\,Fe(CN)_6^{\equiv} + 2\,I^- \rightarrow 2\,Fe(CN)_6^{\overset{=}{=}} + I_2.$$

---

[1] C. R. McCroskey, Dissertation, Columbus, Ohio, 1918; W. C. Vosburgh, J. Am. Chem. Soc. *44*, 2120 (1922); W. C. Bray and H. E. Miller, *ibid.* *46*, 2204 (1924); S. Popoff and J. L. Whitman, *ibid.* *47*, 2259 (1925); F. L. Hahn, *ibid.* *57*, 614 (1935).

Zinc ions yield precipitates with ferrocyanide and ferricyanide; since the precipitate obtained with the former is much less soluble than that with the latter, the addition of zinc sulfate to a ferricyanide solution increases its oxidation potential (p. 577). The zinc ferricyanide precipitate reacts very quickly with iodide to form potassium zinc ferrocyanide, and an equivalent amount of iodine is liberated.

Procedure. Weigh out 1.3 g. of pure potassium ferricyanide and dissolve in 40 ml. of water contained in a glass-stoppered flask. Add 2 g. of potassium iodide, 2 ml. of 4 *N* hydrochloric acid, and stopper the flask. After one minute, add 10 ml. of a 30 per cent zinc sulfate solution, and titrate the mixture containing the gelatinous precipitate with thiosulfate. Add 5 ml. of starch solution after the color has faded to a pale yellow, and continue the titration to the disappearance of the blue color.

Standardization of 0.1 *N* iodine solution against arsenious oxide.

Procedure. If a 0.1 *N* solution of arsenious oxide of accurately known content is available (p. 623), pipet out 25 ml. into a 250 ml. Erlenmeyer flask, add 25 to 50 ml. of water, 1 g. of sodium bicarbonate and a few ml. of starch solution, and titrate with the iodine solution to the first blue color.

Otherwise, weigh out 0.2 g. of pure dry arsenious oxide, dissolve in 10 ml. of 1 *N* sodium hydroxide solution, and add 15 ml. (an excess) of 1 *N* sulfuric acid. Then carefully add 2 g. of sodium bicarbonate dissolved in 50 ml. of water. Titrate with the iodine solution to the first permanent blue tinge, using starch as indicator.

Checking the titer of a thiosulfate solution against standard potassium permanganate.

In the general chapter on Volumetric Analysis it was emphasized that a standardization involves the use of a primary standard substance, and that standardized solutions should not be used in obtaining the normality of another reagent, since errors may accumulate. However, it is good practice to check one standardized solution against another. Thus, the normality of a thiosulfate solution can be compared with that of a potassium permanganate solution:

$$2\,MnO_4^- + 10\,I^- + 16\,H^+ \rightarrow 2\,Mn^{++} + 5\,I_2 + 8\,H_2O.$$

Procedure. Measure out 40 ml. of 0.1 *N* standard permanganate in an Erlenmeyer flask, and add 10 ml. of 2 *N* hydrochloric or sulfuric acid and 3 g. of potassium iodide dissolved in 10 ml. of water. After mixing thoroughly, titrate with thiosulfate, adding starch towards the end of the titration. Calculate the normality of the thiosulfate and compare with the figure found by direct standardization. The normality of a thiosulfate solution can also be checked against a standard iodine solution, and vice versa, as indicated below.

Exercises

I

(a) Titrate 25.00 ml. of 0.1 *N* standard iodine solution with 0.1 *N* standard thiosulfate solution.

(b) As in (a), but add 0.5 g. of sodium bicarbonate to the iodine solution.

(c) As in (a), but add 0.5 g. of sodium carbonate to the iodine solution.

(d) As in (a), but add 5 ml. of 4 *N* hydrochloric acid to the iodine solution.

Report the results and explain any deviations from the calculated value.

II

(e) Titrate 25 ml. of 0.1 *N* sodium thiosulfate solution with 0.1 *N* standard iodine solution.

(f) As in (a), but add 5 ml. of 4 *N* hydrochloric acid to the thiosulfate solution.

Compare the results with the calculated value and explain any deviations.

III

(g) Titrate 25 ml. of 0.1 *N* standard iodine solution with 0.1 *N* standard arsenious oxide solution.

(h) As in (g), but add 2 g. of sodium bicarbonate to the iodine solution.

(i) As in (g), but add 3 g. of borax to the iodine solution.

Report the results, compare them with the calculated values, and explain any deviations found.

Determination of available chlorine in bleaching powder.

1. ***Iodometric method.*** The active constituent of bleaching powder is hypochlorite, which is responsible for the bleaching action of the material. In addition, calcium chloride, calcium chlorate, and calcium oxide are usually present. There is some evidence that the calcium is present in the form of CaCl(OCl), this compound being a derivative of hydrochloric and hypochlorous acids. On treating bleaching powder with acid, chlorine is liberated.

$$\mathrm{CaCl(OCl)} + 2\,\mathrm{H^+} \rightarrow \mathrm{Ca^{++}} + \mathrm{Cl_2} + \mathrm{H_2O}.$$

In the evaluation of bleaching powder the result is usually expressed in terms of available chlorine, which is the chlorine liberated in acidifying the solution.

Available chlorine can be determined iodometrically by adding potassium iodide and acid to the suspension of the material:

$$OCl^- + 2\,I^- + 2\,H^+ \rightarrow Cl^- + I_2 + H_2O.$$

The amount of iodine liberated is equivalent to the available chlorine. In most texts it is recommended that the solution of the sample be acidified with acetic acid. The above reaction is completed quickly at this relatively low acidity. However, it often happens that moist samples of hypochlorite partly decompose on storage, with the formation of chlorite and chlorate. Chlorite in acid medium is reduced by iodide:

$$ClO_2^- + 4\,I^- + 4\,H^+ \rightarrow 2\,I_2 + Cl^- + 2\,H_2O.$$

In acetic acid medium this reaction proceeds very slowly. Therefore if this acid is used for acidifying the hypochlorite-iodide mixture and chlorite is present, no sharp end point is found. The iodine color returns, owing to the slow reaction between chlorite and iodide. For this reason it is better to acidify with sulfuric acid, because in the presence of this acid the chlorite reacts rapidly with the iodide, whereas chlorate does not interfere.

Procedure. Weigh out a 5 g. sample of bleaching powder and triturate it in a mortar with successive portions of water, until it is disintegrated and no lumps remain. Transfer the mixture to a 500 ml. volumetric flask, make up to the mark with water, and shake until a homogeneous suspension is obtained. Pipet out 50 ml. of suspension and transfer to a 250 ml. Erlenmeyer flask. Add 2 g. of potassium iodide and 15 ml. of 4 *N* sulfuric acid, and titrate with standard thiosulfate. Report the percentage of available chlorine in the sample.

2. ***Arsenite method.*** Hypochlorite reacts very quickly with arsenious oxide according to the equation:

$$2\,OCl^- + As_2O_3 \rightarrow As_2O_5 + 2\,Cl^-.$$

No internal indicator is available for the detection of the end point, since hypochlorite is such a powerful oxidizing agent that it destroys all organic dyes. The end point may be found with iodide-starch paper. As long as there is an excess of hypochlorite present, a drop of the solution being titrated turns the iodide-starch paper blue; the end point is reached when a drop of the liquid does not color the indicator paper.

Instead of using an external indicator (the use of which requires some practice) one can add an excess of standard arsenious oxide solution and titrate back with standard iodine solution using starch as indicator. Or, if a standard hypochlorite solution is available, the excess of arsenious oxide can be back-titrated with this solution with Bordeaux as an inside indicator (see p. 586).

Indicator paper. Dip strips of filter paper in 50 ml. of starch solution containing 1 g. of potassium iodide. Drain the strips and spread them on a watch glass to dry. Keep the dried strips in a dark bottle.

Procedure. Transfer 50 ml. of the suspension of bleaching powder (see iodometric procedure) to a 250 ml. beaker. Titrate with standard arsenious oxide solution until no blue color develops when the iodide-starch paper is thoroughly wetted by a drop of the liquid.

Report the percentage of available chlorine in the sample.

Iodide.

Various iodometric methods are available for the determination of iodides. Two simple procedures of great practical importance are described below.

1. *Oxidation of iodide to iodate and iodometric titration of the latter.* Iodide in neutral or weakly acid medium is quantitatively oxidized to iodate by an excess of chlorine or bromine. If much iodide is present, the chlorine or bromine first liberates free iodine, which precipitates but dissolves in an excess of reagent.

$$2\,I^- + 6\,Cl_2 + 6\,H_2O \rightarrow 2\,IO_3^- + 12\,Cl^- + 12\,H^+.$$

The excess of chlorine or bromine may be removed by boiling or by adding an excess of a phenol or aniline solution. A phenol solution is often used for the removal of free chlorine or bromine from a solution. Depending upon the molecular ratio of the phenol and the halogen, mono-, di-, or trichloro (or bromo) phenol and an equivalent amount of halogen acid are formed:

$$\begin{gathered} C_6H_5OH + Br_2 \rightarrow C_6H_4BrOH + H^+ + Br^- \\ C_6H_5OH + 2\,Br_2 \rightarrow C_6H_3Br_2OH + 2\,H^+ + 2\,Br^- \\ C_6H_5OH + 3\,Br_2 \rightarrow C_6H_2Br_3OH + 3\,H^+ + 3\,Br^-. \end{gathered}$$

After the excess of chlorine or bromine has been removed, the iodate formed is titrated iodometrically:

$$IO_3^- + 5\,I^- + 6\,H^+ \rightarrow 3\,I_2 + 3\,H_2O.$$

Since 1 mole of iodide yields 1 mole of iodate and the latter corresponds to 6 equivalents of iodine, it is evident that the equivalent weight of the iodide in this particular titration is $\frac{1}{6}$ of the molecular weight.

The method has the practical advantage that small amounts of iodide yield relatively large amounts of iodine.

Determination of iodide in iodized salt. Iodized table salt usually contains approximately 0.02 per cent of potassium iodide. Since the amount of iodide present is so small, it is necessary to take a large sample and to use 0.005 N sodium thiosulfate to titrate the iodine formed by following the method described above.

Procedure.[1] Dissolve a 5 g. sample of the iodized salt in 100 ml. of water in a 250 ml. Erlenmeyer flask, add a drop of methyl orange indicator, acidify carefully with 2 N sulfuric acid, and add 2 ml. in excess. Introduce bromine vapor just above the surface of the solution with gentle swirling until the solution retains a permanent yellow color (or add freshly prepared bromine water). Add a few glass beads to prevent bumping and boil the solution until the yellow color due to bromine disappears and then for two minutes longer. Cool, wash down the sides of the flask, and add 0.2 g. of potassium iodide and 2 to 3 ml. of starch solution. Mix the contents of the flask, and titrate the liberated iodine immediately with 0.005 N thiosulfate.

Calculate the percentage of potassium iodide in the salt.

NOTES:

1. Bromine vapor is introduced into the flask by blowing a slow current of dried air through a small amount of pure bromine[2] contained in a small gas-washing bottle. The delivery tube from the bromine bottle should end just above the surface of the solution in the flask and should be drawn out to a small tip to prevent the introduction of too large quantities of bromine.

2. Small amounts of bromide (less than 20 times the amount of iodide) do not interfere in the determination. Too little iodine is found when excessive quantities of bromide are present. Quantities of ferric iron in excess of 0.1 mg. interfere, but the interference may be eliminated by the addition of phosphoric acid. Even small amounts (1 mg.) of nitrites interfere, but the interference may be eliminated by the azide method of Reith.[3]

2. *Oxidation of iodide to iodine with sodium nitrite solution.*

Nitrite oxidizes iodide quantitatively to iodine in acid medium:

$$2\,NO_2^- + 2\,I^- + 4\,H^+ \rightarrow 2\,NO + I_2 + 2\,H_2O.$$

In this case the equivalent weight of the iodide is equal to the molecular weight. The liberated iodine can be titrated with standard thiosulfate after removal of the excess of nitrous acid and nitric oxide, both of which would otherwise interfere (p. 617). Both the nitrous acid and the nitric oxide can be destroyed by the addition of an excess of urea, which is oxidized to nitrogen, carbon dioxide, and water; nitrous acid is reduced to nitrogen and water. The reaction between nitrite and iodide in acid medium is rapid, whereas the reaction between the nitrous acid (and also the nitric oxide) and urea is fairly slow. The urea can therefore be added to the acidified iodide solution before the nitrite; the latter reacts first with the iodide; the excess nitrous acid and nitric oxide formed are made harmless by subsequent shaking with the urea. Chlorides do not interfere in this determination, but high results are found if more than an equivalent amount of bromide (with respect to iodide) is present.

---

[1] J. F. Sadusk, Jr. and E. G. Ball, Ind. Eng. Chem., Anal. Ed. *5*, 386 (1933).

[2] G. M. Karns and H. C. Donaldson, J. Am. Chem. Soc. *54*, 442 (1932).

[3] J. F. Reith, Rec. trav. chim. *48*, 386 (1929).

Procedure. Prepare 250 ml. of a solution 0.1 to 0.15 M with respect to iodide. Transfer 25 ml. to a 250 ml. glass-stoppered flask (iodine flask), and add 1 g. of urea, 8 ml. of 0.5 M sodium nitrite solution, and 5 ml. of 4 N sulfuric acid. Stopper the flask and allow to stand with frequent shaking for about ten minutes. Add 2 g. of potassium iodide to dissolve the iodine, and titrate with standard thiosulfate solution. Shake the contents well to dissolve iodine in the gas phase. Report the percentage of iodine in the sample.

Hydrogen peroxide.

Hydrogen peroxide reacts with iodide in acid medium according to the equation:

$$H_2O_2 + 2\,I^- + 2\,H^+ \rightarrow I_2 + 2\,H_2O.$$

The reaction is fairly slow, but it is hastened by molybdate.

Procedure. Dilute a commercial sample of hydrogen peroxide according to the directions given under the permanganimetric procedure (p. 604). Pipet a 25 ml. portion into a 250 ml. Erlenmeyer flask; add 10 ml. of 4 N sulfuric acid, 1 g. of potassium iodide, and 3 drops of a neutral 3 per cent ammonium molybdate solution; and titrate with standard thiosulfate, using starch as indicator.

NOTES:

1. Other peroxides soluble in acid, such as sodium, alkaline earth, and zinc peroxides, may be determined by the above procedure; percarbonates and perborates may likewise be determined in this way.

2. Higher oxides of manganese (pyrolusite) and of lead which are insoluble in acid react very slowly with iodide. Therefore if the determination is made according to the above procedure, the mixture must be allowed to stand a long time before all of the higher oxide is dissolved. This will introduce a material error because of air oxidation of the hydrogen iodide unless special precautions are taken (see p. 617). Therefore it is better to make use of the fact that the higher oxides of manganese and lead oxidize hydrochloric acid to chlorine and hydrobromic acid to bromine. The sample is heated in a distillation apparatus with hydrochloric acid, and the chlorine evolved is absorbed in a potassium iodide solution. The liberated iodine is titrated with thiosulfate. Since the procedure described on page 604 is simpler and more accurate, no detailed directions are given here.

Iodometric determination of copper.

In neutral or weakly acid solutions cupric copper reacts with iodide to give insoluble cuprous iodide and iodine:

$$2\,Cu^{++} + 4\,I^- \rightleftarrows 2\,CuI + I_2.$$

Under proper conditions the reaction runs quantitatively to the right, and copper can be determined iodometrically in this manner by titrating the liberated iodine with thiosulfate. The iodometric method for copper rivals the electrolytic method in accuracy and is more rapid and less subject to interference from other elements.

The reaction between cupric ions and iodide is reversible. Any conditions that lead to an increase in the solubility of cuprous iodide or to a decrease in the concentration of cupric ion (formation of complex or slightly ionized cupric salts, etc.) may prevent the quantitative reduction of cupric copper. A reasonable excess of iodide is always added to insure the complete reduction of copper. The acidity of the solution must be adjusted within certain limits. If the pH of the medium is too high, the reaction does not proceed quantitatively to the right (equation above), and the reaction is slow. Under these conditions a fleeting end point is obtained, the blue color of starch-iodine returning soon after the decolorization by thiosulfate as the equilibrium is shifted to the right. However, for reasons that will be mentioned immediately, it is desirable to maintain the pH of the solution at as high a value as possible consistent with quantitative reduction of copper. To maintain the acidity of the solution at the proper value, a buffer is added. The upper pH limit is determined by the kind of buffer system employed, e.g., the reduction of cupric ions is complete at a higher pH in the case of a phthalate buffer solution than in a phosphate mixture. These differences are due to the different activities of cupric ion in various solutions. The acidity of the reaction mixture must not be too high, or else the results will be slightly high owing to the air oxidation of iodide; copper catalyzes this reaction. Moreover, in too strongly acid solutions there is interference from such elements as arsenic and antimony.

The most common elements found associated with copper in nature which interfere in the method, and which must be rendered inactive, are iron, arsenic, and antimony. Ferric iron is reduced by iodide:

$$2\,Fe^{+++} + 2\,I^- \rightleftarrows 2\,Fe^{++} + I_2.$$

The interference of iron can be prevented by transforming it into a complex that will not react with iodide in slightly acid solutions. Alkali pyrophosphates and fluoride are commonly used for this purpose. The latter, which is preferable, gives the slightly dissociated ion $FeF_6^{\equiv}$. When added in the form of ammonium bifluoride, the iron is made harmless, and moreover the pH is adjusted t the correct value (hydrogen fluoride mixed with fluorides gives buffer system). Arsenic and antimony must not be present in th trivalent form, for these consume iodine. These elements will generally be present in the quinquevalent form as a consequence o the oxidizing attack used to bring the sample into solution. Arsenic and antimony in the quinquevalent form will not oxidize iodide i a medium having a pH greater than 3.5. By buffering the solution with ammonium bifluoride as described below, it is possible to prevent the interference of these elements and still maintain the pH of the solution at a value at which the reduction of cupric ion is complete. Oxidizing agents such as the oxides of nitrogen and free bromine, possibly remaining after bringing the sample into solution, must be expelled. Elements such as silver, lead, bismuth, and zinc do not interfere, at least if present in relatively small amounts, as is usually the case.

In neutral solution cupric copper does not react with iodide if it is transformed into a tartrate complex by the addition of sodium potassium tartrate. Use is made of this behavior when trivalent arsenic must be titrated with iodine in the presence of copper (for example, in the analysis of "Paris green"). The bright-blue solution containing an excess of tartrate is titrated with standard iodine solution. At the end point the color changes sharply to greenish-blue (starch indicator need not be added). It is possible to titrate the copper in the same solution after the arsenic titration, after adding sulfuric acid to give the proper acidity.

The iodometric copper titration is extensively applied in the determination of reducing sugars (dextrose, levulose, etc.). These are oxidized at boiling temperature by an alkaline solution of cupric copper containing tartrate or citrate to hold the metal in solution (complex formation), the copper being reduced to cuprous oxide, which is precipitated. The precipitate may be filtered off and weighed, or more conveniently (1) it may be dissolved and oxidized, and the copper determined iodometrically, or (2) the excess of copper remaining in solution may be determined iodometrically after acidification. The reaction between the reducing sugar and the copper is not stoichiometric, the amount of cuprous oxide precipitated by a given sugar depending upon such factors as the concentration of the sugar solution, the composition of the reagent, and the time of boiling. Therefore the amount of sugar corresponding to a given weight of cuprous oxide must be found by reference to a table which has been constructed empirically. The procedure used in the construction of the table must be carefully followed in the determination.

Determination of copper in ores. The following rapid method for copper in ores, mattes, slags, etc., is due to Park.[1] The presence of iron, arsenic, and antimony is provided for. The sample is brought into solution by treatment with hot nitric acid, which oxidizes these elements, as well as any cuprous copper present, to their highest valences. The interference of iron is prevented by transforming it into complex ferric fluoride. By addition of the proper amount of ammonium bifluoride the pH is adjusted to a value of 3.3 to 4.0.[1] At this acidity there is no interference from quinquevalent arsenic or antimony.

---

[1] B. Park, Ind. Eng. Chem., Anal. Ed. 3, 77 (1931)

Procedure. Weigh out 1 g.[2] of finely ground material into a 150 ml. beaker, add 20 ml. of concentrated nitric acid, and warm until it is certain that all the copper has been brought into solution. Evaporate the solution to a volume of 5 ml., add 25 ml. of water, and boil to bring all soluble material into solution and to expel the oxides of nitrogen. Filter off the residue on a small filter paper, receiving the filtrate in a 250 ml. Erlenmeyer flask (if the residue is small in amount and light-colored, the filtration may be omitted). Wash the residue thoroughly with hot 1 per cent nitric acid. Concentrate the filtrate to 25 ml., cool, and add dropwise dilute ammonium hydroxide to precipitate all the iron, being careful to avoid an excess; the liquid should smell very faintly of ammonia after blowing away the fumes. Add 2.0 g. of ammonium bifluoride and shake to dissolve the ferric hydroxide, and then add 3 g. of potassium iodide. Titrate the liberated iodine at once with 0.1 N sodium thiosulfate (Note 2), adding 3 ml. of 0.2 per cent starch solution near the end point. The color change is from blue to yellowish-white. The blue color should not return within ten or fifteen minutes. A quick return of the color may be caused by the addition of too much ammonium hydroxide or too little fluoride, as well as by the presence of oxides of nitrogen. Report the percentage of copper.

NOTES:

1. Most copper ores can be decomposed by heating with concentrated nitric acid. If such treatment fails to bring all the copper into solution, heating with hydrochloric and nitric acid followed by evaporation to fumes with sulfuric acid, dilution, and boiling with bromine water to reoxidize any arsenic or antimony that may have been reduced by free sulfur will usually bring all the copper into solution. All bromine must, of course, be expelled by boiling

---

[1] Park also added potassium biphthalate for the adjustment of pH. According to W. R. Crowell, T. E. Hillis, S. P. Rittenberg, and R. F. Svenson, Ind. Eng. Chem., Anal. Ed. *8*, 9 (1936), the addition of the biphthalate can be omitted since the bifluoride has the proper buffering action.

[2] This is the proper weight of sample for material containing 10 to 30 per cent of copper; for lower contents take a larger amount.

before adding iodide. Some silicate ores of copper and slags may not be completely decomposed by acid treatment. In such a case the acid-insoluble material must be fused with sodium carbonate after extraction with ammonium acetate and ammonium hydroxide solutions to remove any lead sulfate and silver chloride, respectively, that may be present, which would otherwise attack the platinum crucible.

2. Although not strictly necessary, it is preferable to standardize the thiosulfate solution against pure copper:

Dissolve 0.20 to 0.25 g. of pure electrolytic copper foil in 10 ml. of 6 *N* nitric acid, and evaporate the solution to the point at which it will solidify on cooling, but not further, or basic salts of copper may be formed that will be hard to dissolve. Dissolve the copper nitrate in 25 ml. of water, and add dropwise a 1 *N* solution of sodium hydroxide until a slight permanent precipitate is obtained. Add 7 ml. of 6 *N* acetic acid to the liquid and dilute to 50 ml. with cold water. To the cool solution add 3 g. of potassium iodide, stir or shake to dissolve, and titrate with the 0.1 *N* sodium thiosulfate solution, adding starch when the color of the iodine has become pale yellow.

3. Approximately 1 g. of ammonium bifluoride should be added for each 0.1 g. of iron present. Aluminum forms a slightly soluble complex fluoride, so that if it is present in any quantity, more bifluoride must be added to take the place of the fluoride bound by this metal. Manganese when present alone does not interfere in the method, but if iron is present with manganese high results are obtained. A few milligrams of manganese with 0.1 to 0.2 g. iron lead to no serious error; when larger amounts are present (which rarely happens), iron must be removed before the titration.

Other iodometric and iodimetric methods.

It is beyond the scope of this text to consider all iodometric and iodimetric procedures.[1] However, the principal reactions on which a number of determinations are based are given briefly below:

Hydrogen sulfide. Hydrogen sulfide in acid medium is oxidized to sulfur by iodine:

$$H_2S + I_2 \rightarrow S + 2\,H^+ + 2\,I^-.$$

The solution must not be alkaline (alkali sulfides), for part of the sulfide is then oxidized to sulfate:

$$S^= + 4\,I_2 + 8\,OH^- \rightarrow SO_4^= + 8\,I^- + 4\,H_2O.$$

The hydrogen sulfide titration is often used to determine sulfur in iron and steel (see Chapter XLI) and the dissolved gas in mineral waters.

Sulfurous acid and its salts.

$$\begin{aligned} HSO_3^- + I_2 + H_2O &\rightarrow SO_4^= + 2\,I^- + 3\,H^+ \\ SO_3^= + I_2 + H_2O &\rightarrow SO_4^= + 2\,I^- + 2\,H^+. \end{aligned}$$

---

[1] Cf. I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis*, Vol. II.

The method is not accurate, since low results are obtained as a result of air oxidation of the sulfurous acid or its salts during the titration.

Tin. Quadrivalent tin is reduced by metallic iron, lead, or zinc to the bivalent form

$$Sn^{++++} + Fe \rightleftarrows Fe^{++} + Sn^{++}$$

and the latter may be titrated in acid medium with iodine. Stannous tin is easily oxidized by air, especially during the titration. Therefore air oxidation must be prevented by working in an atmosphere of carbon dioxide.

Ferric iron.

$$2\,Fe^{+++} + 2\,I^- \rightarrow 2\,Fe^{++} + I_2.$$

The equilibrium in acid medium is displaced to the right by using a very large excess of potassium iodide. The method is not of much practical significance for the determination of iron, since titration with permanganate, dichromate, or ceric sulfate, after reduction of the ferric iron to the ferrous state, is much more accurate.

PROBLEMS

1. A sample of calcium hypochlorite was found to contain 50 per cent of available chlorine. How many grams of a 3 per cent solution of hydrogen peroxide are required to reduce all the hypochlorite in 10 grams of the sample if the reaction takes place according to the equation:

$$OCl^- + H_2O_2 \rightarrow Cl^- + H_2O + O_2?$$

What is the volume of the oxygen evolved at 25° and 760 mm. pressure?
Ans. 79.8 g.; 1.725 liters.

2. How could trivalent arsenic be determined iodimetrically in a solution containing potassium chromate?

3. The lead in 25 ml. of a solution is precipitated with an excess of potassium chromate; the precipitate of lead chromate is filtered off, washed, dissolved in acid, and titrated iodometrically. (Give equations.) 31.50 ml. of 0.1010 N sodium thiosulfate are required to titrate the liberated iodine. What is the molarity of the solution with respect to lead? *Ans.* 0.0424 M.

4. 0.2000 g. of sodium oxalate requires 31.00 ml. of potassium permanganate solution for complete oxidation in acid solution. How many ml. of 0.1000 N sodium thiosulfate will be required in the iodometric titration of 25 ml. of this permanganate solution? Give equations. *Ans.* 24.07 ml.

5. A solution of chromic acid containing iron is to be titrated iodometrically. How can the iron be made harmless?

6. 25.00 ml. of a potassium iodide solution are treated with dilute hydrochloric acid and 10.00 ml. of 0.0500 M potassium iodate solution (an excess). The iodine liberated is volatilized by boiling the solution, and after cooling an excess of potassium iodide is added to react with the iodate remaining. 21.14

ml. of 0.1008 *N* sodium thiosulfate solution are required to titrate the lib
iodine. Calculate the molarity of the potassium iodide solution. *Ans.* 0

7. To 25.00 ml. of a potassium iodide solution an excess of potassium
and 1 g. of a weak acid are added. The iodine formed (give reaction equ
is titrated with thiosulfate. How may the acidity be adjusted? Und
proper conditions of titration 30.00 ml. of 0.1048 *N* thiosulfate are used. C
late the iodide content of the solution. *Ans.* 0.10

8. A solution contains cupric copper, trivalent arsenic, and ferric iron.
can one determine iodometrically the arsenic and the copper in the mix
(The oxalate complex of cupric copper does not react with iodide in ne
medium.)

CHAPTER XL

POTASSIUM BROMATE AND CALCIUM HYPOCHLORITE AS STANDARD REAGENTS

Potassium bromate as an oxidizing agent.

For a general discussion see page 585.

Standard potassium bromate solution is an excellent reagent for the determination of trivalent arsenic and antimony, thallous thallium, and hydrazine in acid medium. Cuprous copper and stannous tin may also be determined if air is excluded.

$$BrO_3^- + 3\,As^{3+} + 6\,H^+ \rightarrow Br^- + 3\,As^{5+} + 3\,H_2O$$
$$BrO_3^- + 3\,Tl^+ + 6\,H^+ \rightarrow Br^- + 3\,Tl^{+++} + 3\,H_2O$$
$$BrO_3^- + 6\,Cu^+ + 6\,H^+ \rightarrow Br^- + 6\,Cu^{++} + 3\,H_2O$$
$$2\,BrO_3^- + 3\,N_2H_4 \rightarrow 2\,Br^- + 3\,N_2 + 6\,H_2O.$$

The equivalent weight of potassium bromate is $\frac{1}{6}$ of the molecular weight.

It has already been mentioned that the indicators used, such as methyl orange, the sodium salt of methyl red (solution in *water*), Bordeaux, and the indigo sulfonic acids, are irreversibly oxidized by an excess of bromate. Therefore if an excess of bromate is accidentally added, it cannot be back-titrated directly using these ndicators. In such a case an excess of standard arsenious oxide s added, which is then titrated with the bromate.

In the titration of arsenic and antimony the solution should be at least 1.5 *N* with respect to hydrochloric acid at the end point.

Preparation of 0.1 *N* standard potassium bromate solution.

Weigh out 2.783 g. of pure potassium bromate which has been dried at 150°, and dilute with water to 1 liter.

Titration of standard arsenious oxide solution against standard bromate.

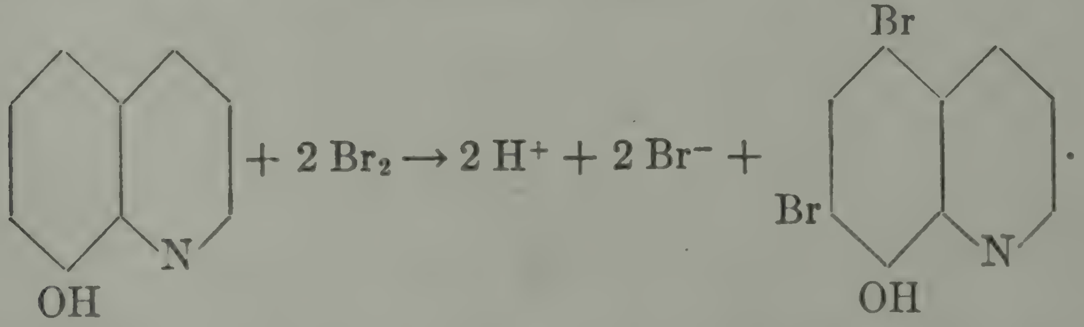
Procedure. Pipet 25 ml. of standard 0.1 *N* arsenious oxide soluon (p. 623) into an Erlenmeyer flask and add 25 ml. of water, 5 ml. of concentrated hydrochloric acid, 0.5 g. of potassium bromide, and 1 to 2 drops of 0.1 per cent solution of methyl orange. Titrate slowly with the standard potassium bromate solution with constant swirling. Near the end point add the bromate dropwise with intervals of a few seconds between drops until the color changes sharply from red to colorless or very pale yellow. Add another drop of indicator to make sure that the end point has been reached. If the color of the indicator fades before the end point is reached, owing to too rapid titration and insufficient mixing, add another drop of methyl orange so that the solution assumes a distinct pink color; then continue the titration. Compare the volume of bromate used with the calculated volume.

Use of potassium bromate in bromine substitution reactions.

See page 586.

Determination of metals yielding slightly soluble compounds with 8-hydroxyquinoline.

Various metals such as aluminum, iron, zinc, nickel, cobalt, copper, manganese, and magnesium under specified conditions of acidity or alkalinity yield well-defined crystalline precipitates with 8-hydroxyquinoline (p. 79 and p. 587). Use is made of these precipitations in gravimetric determinations (p. 327 and p. 373). The 8-hydroxyquinoline in the precipitates can also be determined by bromometric titration. The volumetric method is of special advantage when small amounts of the metals are to be determined. The precipitates obtained with 8-hydroxyquinoline have the general formula $(C_9H_6ON)_nMe$, in which n is the valence of the metal. In the bromometric determination of hydroxyquinoline in acid medium, 1 mole of the latter requires 4 equivalents of bromine:



Therefore 1 millimole of a divalent metal in the oxine precipitate requires 8 milliequivalents of bromine; and 1 millimole of a trivalent metal, 12 milliequivalents.

Determination of magnesium.

Procedure. Precipitate magnesium with 8-hydroxyquinoline from a solution containing 8 to 12 mg. of magnesium, and wash the precipitate, proceeding as described on page 373. Dissolve the precipitate on the filter in 2 to 2.5 N hydrochloric acid, collecting the filtrate in a glass-stoppered flask; and wash the filter with the same acid until the washings are colorless. Adjust the volume of the filtrate with the same acid to 50 to 75 ml., add 1 g. of potassium bromide and 2 to 4 drops of a 0.1 per cent solution of the sodium salt of methyl red. Titrate slowly with standard bromate solution, swirling constantly, until the color changes from red to yellow. A slight but distinct excess of bromine is then present. Stopper the flask, allow to stand for two minutes, add 1 g. of potassium iodide, and titrate the liberated iodine with standard 0.1 N sodium thiosulfate, using starch as indicator (p. 623).

The direct titration of the dissolved precipitate with bromate does not give accurate results, since it is hard to detect the end point. However, the addition of the indicator is recommended because it permits the detection of a slight excess of bromine. The indicator blank is negligibly small.

Upon the addition of potassium iodide to the solution a chocolate-brown precipitate of an iodine addition compound of the dibromohydroxyquinoline is formed, which, however, decomposes rapidly on titration with thiosulfate.

Instead of back-titrating iodometrically, an excess of standard arsenious oxide may be added and the excess of the latter titrated directly with standard bromate (see p. 637).

Calcium hypochlorite as an oxidizing agent.

See page 587.

One-tenth normal calcium hypochlorite solution has been proposed by Kolthoff and Stenger[1] as a standard oxidizing agent, since it has been found that the solution prepared from a commercial product[2] can be kept in dark glass bottles for a long time without appreciable change in titer.

Preparation of approximately 0.1 N solution. Six to ten grams of calcium hypochlorite, depending upon the amount of available chlorine in the commercial product, are added to 250 ml. of distilled water, the mixture is shaken and the solution filtered to remove iron oxide, excess of calcium hydroxide, and any other insoluble material present in the commercial product. The filtrate is diluted to one liter. The formation of a turbidity on standing as the result of the precipitation of calcium carbonate is of no consequence. The standard solution should be kept in a glass-stoppered bottle and protected from the light (the bottle may be painted black on the outside).

Composition of the standard solution. An analysis of an approximately 0.1 N hypochlorite solution (prepared from the above product) gave the following composition: hypochlorite, 0.1068 N; calcium, 0.0743 N; sodium, 0.0306 N; free hydroxide, 0.0037 N; chloride, 0.0478 N. This corresponds to $Ca(OCl)_2$, 0.0267 M; $Ca(OH)_2$, 0.0019 M; $CaCl_2$, 0.0086 M; and NaCl, 0.0306 M.

---

[1] I. M. Kolthoff and V. A. Stenger, Ind. Eng. Chem., Anal. Ed. 7, 79 (1935).

[2] Manufactured by the Mathieson Alkali Co., Niagara Falls, N. Y.

Stability of the standard solution. When kept in a dark bottle and in a dark compartment, it was found that the normality of various solutions decreased 0.0 to 0.3 per cent after three months, 0.3 to 0.5 per cent after six months, and 0.3 to 1 per cent after one year. More dilute solutions (0.01 N) are less stable.

Standardization of the hypochlorite solution against arsenious oxide. Indicator solution: 0.2 per cent Bordeaux (British Colour Index No. 88). Color change from pink to very faint yellow-green. An indicator correction of 0.03 ml. of 0.1 N hypochlorite should be subtracted per 0.1 ml. of indicator solution in a final volume of 50 to 75 ml.

Procedure. Pipet 25 ml. of standard 0.1 N arsenious oxide solution into an Erlenmeyer flask; add 1 g. of potassium bromide and 0.5 g. of sodium or potassium bicarbonate. Titrate with 0.1 N hypochlorite solution, added moderately rapidly until within a few ml. of the expected end point. Add one drop of indicator, and then titrate dropwise with constant swirling until the color of the indicator fades. Add one more drop of indicator; if the color does not fade, continue the titration until one drop of hypochlorite causes the solution to flash from pink to colorless or light yellow-green. Subtract the indicator correction, and calculate the normality of the hypochlorite solution.

NOTES:

1. Since the indicator reaction is not reversible, one must be sure that the end point is actually reached when the color has faded; this can be tested by adding more indicator. It is advantageous, however, to use as little indicator as possible. When the approximate end point is known, one can perceive the end point with only one drop of Bordeaux solution.
2. The solution can also be standardized iodometrically. For 25 ml. of hypochlorite solution add 1 to 1.5 g. of potassium iodide, 5 ml. of 6 N sulfuric acid, and titrate with standard sodium thiosulfate.

Determination of ammonia in ammonium sulfate.

In the presence of sodium bicarbonate and bromide (p. 587), ammonia is oxidized quantitatively to nitrogen and water by calcium hypochlorite.

$$2\,NH_3 + 3\,OBr^- \rightarrow N_2 + 3\,Br^- + 3\,H_2O.$$

It is necessary to add an excess of hypochlorite since the reaction is fairly slow. Then a known excess of arsenious oxide solution is added, and the latter is back-titrated as described above.

Procedure. Weigh out a 1 g. sample of ammonium sulfate, dissolve in water, and make up to the mark in a 250 ml. volumetric flask. Pipet out 25 ml. of this solution, add 1 g. of potassium bromide and 0.5 g. of sodium or potassium bicarbonate, and titrate with 0.1 N hypochlorite solution until a permanent light-yellow color, indicating a slight excess of hypobromite, appears.

Allow to stand five minutes, and then add from a pipet 10 ml. of 0.01 N arsenious oxide (obtained by proper dilution of the standard 0.1 N solution). Add one drop of Bordeaux indicator, which should impart a pinkish color to the solution. (If the color fades, there is not an excess of arsenious oxide present.) Continue the titration with hypochlorite as in the standardization of the latter against arsenious oxide.

Calculate the amount of hypochlorite corresponding to 10 ml. of 0.01 *N* arsenious oxide solution, and deduct this volume from the total volume of hypochlorite used. The difference is equivalent to the amount of ammonia present. Calculate the percentage of NH_3 and of N.

NOTE:

The excess of hypochlorite (or actually hypobromite) may also be determined iodometrically by adding first 0.5 g. of potassium iodide, then 10 ml. of 6 *N* H_2SO_4 (slowly to avoid vigorous effervescence), and finally titrating with standard thiosulfate. The advantage in the use of arsenious oxide in bicarbonate medium is that interference of foreign oxidizing agents such as ferric iron, chromate, or arsenate is eliminated. On the other hand, the presence of iodide will cause an error in the arsenious oxide procedure but not in the iodometric method.

PHYSICO-CHEMICAL METHODS

CHAPTER XLI

COLORIMETRY AND SPECTROPHOTOMETRY

Introduction.

Photometric chemical analysis embraces *colorimetry*, *spectrophotometry*, and *nephelometry* (see p. 687). Photometric chemical analysis may be defined as analysis which in general is based upon the measurement of the amount of light absorbed by a colored solution (*colorimetry*, *spectrophotometry*) or by a white suspension (*turbidimetry*, see p. 688) or of the amount of light scattered by a suspension (*nephelometry*, see p. 688). The concentration of a colored substance in a solution can be determined directly by colorimetric or spectrophotometric analysis; if the substance to be determined is colorless, it may often be transformed into a colored compound by some suitable chemical reaction. In nephelometric or turbidimetric analyses the substance to be determined is transformed into an insoluble compound which remains in suspension.

In colorimetry, natural or artificial white light (continuous spectrum between red and ultraviolet) is used as a light source. The measurements are made with a simple instrument called a *colorimeter*. In spectrophotometry, light of a definite wave length is used as a light source; the instrument used in the measurements is much more complicated than the colorimeter and is called a spectrophotometer. With a suitable instrument of the latter type measurements can also be made in the ultraviolet and infrared regions of the spectrum, where ordinary colorimetric measurements are impossible.

With the aid of suitable light filters it is possible to obtain from white light, in a simple way, light of a definite color, exhibiting a narrow range of wave lengths. Use is made of light filters in several colorimeters and abridged spectrophotometers.

The primary advantage of colorimetric methods is that traces of substances can be determined in a simple way, whereas gravimetric and volumetric procedures would yield relatively great errors with such amounts, since the absolute amounts of the substances to be determined are so small. The colorimetric method therefore is especially suitable for the determination of micro and semi-micro quantities of constituents. For the analysis of macro quantities gravimetric and volumetric procedures generally are preferable, since they are more accurate. It should be well understood that even in the most favorable cases, ordinary colorimetric methods do not yield an accuracy greater than about 2 per cent. Considering, however, the rapid development of optical methods of analysis (use of photoelectric and photronic cells), it is not too optimistic to expect that colorimeters and spectrophotometers may be developed in the future to such a degree of perfection that the error will be reduced to a few tenths of a per cent. If this is true, it may be expected that photometric analyses may compete with gravimetric and volumetric analyses as far as accuracy is concerned; in addition the former, as a rule, have the great advantages of being more simple and economical as far as time is concerned. Even if the instrumental error can be reduced to a small figure, it is of importance to consider the methodic error which may be very small or large. This will be clear from a discussion of the theory of colorimetry and spectrophotometry given in the following pages.

Theory of colorimetry and spectrophotometry.

When a beam of monochromatic light falls on a homogeneous layer of a substance, part of the light is reflected, part is absorbed, and part is transmitted. If the intensity of the original light is equal to I_o, that of the reflected light to I_r, that of the absorbed light to I_a, and that of the transmitted light to I_t, we have the following relation:

$$I_o = I_r + I_a + I_t.$$

In most cases I_r can be neglected, hence

$$I_o = I_a + I_t.$$[1]

Lambert (1760) was the first to investigate the relation between the intensities of the incident and transmitted light. Later, Beer (1852) made similar investigations for solutions. Colorimetry and spectrophotometry are based upon the laws of Lambert and of Beer.

Laws of Lambert.[2]

1. The amount of monochromatic light absorbed by a body is proportional to the intensity of the incident light or, expressed in other words, the ratio of the intensities of the transmitted (I_t) and incident light (I_o) is constant:

$$I_t = I_o a \quad \text{or} \quad \frac{I_t}{I_o} = a. \tag{1}$$

The factor a gives the fraction of the incident light which is transmitted by a layer 1 cm. in thickness. This factor is often called the *transmission coefficient.*

---

[1] According to Fresnel, the following relation exists between I_o and I_r:

$$I_o - I_r = I_o(1 - R)$$
$$R = \left(\frac{n-1}{n+1}\right)^2$$

in which n denotes the refractive index of the substance.

In colorimetry and spectrophotometry we are usually dealing with aqueous solutions, and it is easily shown that $(1 - R)$ will differ very little from 1. This is no longer true when we are dealing with solids, especially if they have a high reflecting power (metals, dyestuffs), or with colored suspensions.

[2] Lambert, *Photometria sive de mensura et gradibus luminis, colorum et umbrae* (1760); for a detailed review of the derivation of the equations see, e. g., P. Karsten, Thesis, Groningen (1934).

2. The intensity of the transmitted light decreases in geometric progression when the thickness of the layer through which the light travels increases in arithmetic progression. This means that layers of the same thickness of the same substance absorb the same fraction of the incident light. According to the second law, the following relation exists between I_t and I_o:

$$I_t = I_o a^{-l} \tag{2}$$

in which l denotes the length or thickness of the layer. If light of intensity I_o falls on an infinitely thin layer dl of the absorbing medium, the decrease in intensity dI of the incident light is proportional to I_o and dl:

$$dI = -kI_o dl \tag{3}$$

in which k is a proportionality factor.

Integrating equation (3), we find:

$$\int_{I_o}^{I_t} \frac{dI}{I} = -k\int_0^l dl$$

$$ln\frac{I_t}{I_o} = -kl$$

$$I_t = I_o e^{-kl}. \tag{4}$$

The constant k is often called the *absorption index* or the *absorption coefficient.*

Changing from natural to Briggsian logarithms,[1] we have

$$I_t = I_o \cdot 10^{-0.4343kl} = I_o \cdot 10^{-\epsilon' l}. \tag{5}$$

Bunsen and Roscoe[2] called the constant ϵ' the *extinction coefficient.* It is easily seen that ϵ' is the reciprocal value of the thickness of the layer in cm. at which I_t is equal to $\frac{1}{10} I_o$.

$$\frac{I_t}{I_o} = 0.1 = 10^{-\epsilon' l} \quad \text{or} \quad \epsilon' l = 1 \quad \text{and} \quad \epsilon' = \frac{1}{l}.$$

Beer's law. So far we have considered the light absorption and transmission as a function of the thickness of the layer only. In analytical chemistry, however, we are mainly interested in solutions. Beer[3] almost simultaneously with Bernard[4] studied the influence of the *concentration* of the colored substance in the solution upon the light transmission or absorption. They found the same relation between transmission and concentration that Lambert had found between transmission and thickness of the layer.

Mathematically, Beer's law can be formulated by the equation:

$$I_t = I_o a^{-c} \tag{6}$$

[1] $\log_{10} e = 0.4343$.

[2] Bunsen and Roscoe, Ann. Physik. *101*, 235 (1857).

[3] Beer, Ann. Physik. *86*, 78 (1852).

[4] F. Bernard, Ann. chim. phys. [3] *35*, 385 (1852).

in which c denotes the concentration. (When $c = 1$, equation 6 is reduced to equation 1.) Again the following relation holds:

$$dI = -k_1 I_0 dc \tag{7}$$

in which dc denotes an infinitely small change in the concentration. Integration of equation (7) between I_t and I_o gives

$$I_t = I_0 e^{-k_1 c} \tag{8}$$

and

$$I_t = I_0 10^{-0.4343 k_1 c}. \tag{9}$$

Combination of equations (5) and (9) gives the fundamental equation of colorimetry and spectrophotometry:

$$I_t = I_0 10^{-\epsilon l c}. \tag{10}$$

Evidently the value of ϵ depends upon the method of expressing the concentration. If c is expressed as molar concentration, ϵ denotes the *molar extinction coefficient* and is equal to the reciprocal value of the thickness (in cm.) of a 1 molar solution ($c = 1$) at which I_t is 0.1 of I_0.

Expression (8) holds for varying concentration of the colored component if Beer's law is obeyed.

Let us now consider two solutions of a colored substance having concentrations c_1 and c_2. They are placed in an instrument in which the thickness of the layers can be changed and measured easily and which allows comparison of the amounts of transmitted light (colorimeter, see p. 657). When the two layers have the same color intensity or, in other words, when the system is optically balanced, it is evident that

$$I_{t_1} = I_{t_2} = I_0 10^{-\epsilon l_1 c_1} = I_0 10^{-\epsilon l_2 c_2}. \tag{11}$$

Here l_1 and l_2 denote the lengths of the columns of the solutions with concentrations c_1 and c_2 when the system is balanced. Under these conditions, and when Beer's law is obeyed, it is found that

$$l_1 c_1 = l_2 c_2. \tag{12}$$

The colorimeter therefore serves two purposes:

1. It allows an investigation of the validity of Beer's law by changing c_1 and c_2 and determining whether expression (12) holds.
2. It allows the determination of the concentration c_x of a colored solution by comparison with a solution of known concentration c. When the system is optically balanced, the following relation holds:

$$c_x = \frac{l}{l_x} c. \tag{13}$$

l_x is the length of the column of the unknown and l that of the solution with known concentration c. It must be realized that the fundamental equation (12) holds only when Beer's law is obeyed and the instrument has no optical defects.

Deviations from Beer's law. If the structure of the colored ions or of the colored nonelectrolytes in the dissolved state does not change with the concentration, Beer's law will as a rule hold over a wide range of concentrations. For example, this is the case with permanganates, chromates, picrates, and many organic dyes. These salts are strong electrolytes, and the light absorption is governed by the concentration and not by the activity of these ions. The presence of small amounts of colorless electrolytes which do not react chemically with the colored components does not affect the light absorption as a rule. Large amounts of electrolytes may affect the absorption spectrum qualitatively (shift of maximum absorption to another wave length) as well as quantitatively (change of the value of the extinction coefficient). The electrolyte effect is to be attributed to a physical interaction between the ions of the electrolyte and the colored ions or molecules, which results in a deformation of the latter with a consequent change of the light absorption. There may also be an interaction between the added electrolyte, solvent (usually water), and the colored compound, resulting in a change in the degree of solvation (hydration) of the latter with a consequent change in the absorption spectrum. If the state of dissociation of a colored compound changes with the concentration, Beer's law will usually not be obeyed. Electrolytes which react chemically with the colored components affect the absorption spectrum.

In the following, the most important factors responsible for the deviation from Beer's law are briefly discussed.

Dissociation phenomena. If the colored compound A is partly transformed into a form B of different color, Beer's law will be valid under equilibrium conditions if the reaction is reversible:

$$A \rightleftarrows B$$

$$\frac{[B]}{[A]} = K.$$

The ratio of $[A]$ to $[B]$ remains constant and is independent of the concentration. If the compound is in reversible equilibrium with two or more components B, C, etc., Beer's law will not hold:

$$A \rightleftarrows B + C$$

$$\frac{[B][C]}{[A]} = K.$$

This, for example, is the case with picric acid. The undissociated form is colorless in solution, the picrate ions have an intense yellow color, whereas the hydrogen ions are colorless. If α is the degree of dissociation of picric acid, the concentration of the picrate ions is equal to αC, C being the analytical concentration of the acid. Since α increases with decreasing concentration (see Chapter IV), it is clear that the relative color intensity of the solution $\left(\text{determined by } \frac{\alpha C}{C}\right)$ increases with decreasing concentration.

From the effect of the hydrogen-ion concentration upon acid-base equilibria (Chapter IV), it follows that the color of a picric acid solution will change with changing hydrogen-ion concentration. Quite generally this will be true when we are dealing with colored anions of weak acids or colored cations of weak bases (see Chapter XXIX on indicators). The color of chromates is independent of the pH if the latter is greater than 6. At lower pH values, however, the following equilibria must be considered:

$$CrO_4^{=} + H^+ \rightleftarrows HCrO_4^-$$
$$2\ HCrO_4^- \rightleftarrows Cr_2O_7^{=} + H_2O.$$

The chromate ions have a yellow color, whereas the dichromate ions are orange. Therefore the color will change towards orange with increasing hydrogen-ion concentration.

In connection with the above, a few words may be said of the effect of hydrolysis. Consider a solution of ferric chloride or ferric nitrate in water. The ferric ions are strongly hydrolyzed, giving brown hydrous ferric oxide, which stays in colloidal solution:

$$Fe^{+++} + 3\ H_2O \rightleftarrows \underset{(brown)}{Fe(OH)_3} + 3\ H^+.$$

On dissolving a ferric salt in water, the above equilibrium is reached extremely slowly. The freshly prepared solution has a yellow color, which on standing changes to a more intense brown. The final equilibrium is not reached even after half a year. Since the hydrolysis increases very strongly with the temperature, the color of the iron solution will be greatly dependent upon the temperature. The hydrolysis of an iron salt is strongly suppressed by an increase in the hydrogen-ion concentration, as is evident from the hydrolysis equation.[1] Care must be taken in the choice of the acid that is added to iron solutions to prevent hydrolysis, because ferric ions form colorless complexes with several anions (*vide infra*).

Complex formation. Some salts have a tendency to form complexes whose colors are different from those of the simple compounds:

$$n\,A \rightleftarrows \underset{(complex)}{(A)_n}$$
$$\frac{[(A)_n]}{[A]^n} = K.$$

The degree of complex formation decreases with increasing dilution, and therefore Beer's law does not hold. A well-known example which demonstrates the effect of complex formation upon the color is found in the case of cobalt chloride:[2]

$$\underset{(pink)}{2\ CoCl_2} \rightleftarrows \underset{(blue)}{[CoCl_4]Co}.$$

A concentrated solution of cobalt chloride has a blue color, which changes to pink on dilution. Quite generally complex formation affects the color of a colored compound. Aquo-cupric ions, $Cu(H_2O)_4^{++}$, are a light blue; the corresponding ammonio-cupric ions, $Cu(NH_3)_4^{++}$, are a dark blue. Intermediate between these two, depending upon the ammonia concentration and the temperature, other complexes, $Cu(NH_3)_3H_2O^{++}$, $Cu(NH_3)_2(H_2O)_2^{++}$, etc., with different extinction coefficients, may exist. The final equilibrium is very complicated and has to be considered in the colorimetric copper determination in ammoniacal medium.

---

[1] See, e.g., M. G. Mellon and C. T. Kasline, Ind. Eng. Chem., Anal. Ed. 7, 187 (1935).

[2] See A. Hantzsch and Y. Shibata, Z. anorg. allgem. Chem. 73, 309 (1912)

Use is also made of complex formation in the colorimetric iron determination in about 25 per cent hydrochloric acid. In this medium all the ferric iron is present as a complex, $FeCl_6^{\equiv}$, which possesses an intense yellow color.

Sometimes it is possible to transform a colored ion into a colorless complex and thus prevent its interference in the colorimetric determination of another constituent. Ferric ions, for example, form colorless complexes with fluoride, phosphate, and pyrophosphate; and therefore one of these is often used to eliminate the interference by ferric iron in the colorimetric determination of other elements (e.g., manganese).

Colored suspensions. So far we have considered only true ionic or molecular dispersions of the solute. In colorimetry use is often made of the fact that a constituent can be easily transformed into an intensely colored but insoluble compound which remains in suspension (ammonia with Nessler's reagent; heavy metals with sulfide). The theory of light absorption by colored suspensions is extremely complicated (see a discussion of white suspensions, p. 689). The color of the suspension depends largely upon the size of the suspended particles. The latter factor in turn depends upon:

1. The concentration of the reacting components.
2. The temperature of preparation of the suspension.
3. The time of standing after the addition of the reagent.
4. The presence of other electrolytes. The latter have a coagulating effect upon the suspension (p. 95), thereby agglomerating the particles. If the particles settle too quickly, a colorimetric comparison is impossible. In such cases a protective colloid is often added to stabilize the suspension.

From the above, it is evident that in colorimetric work with suspensions the conditions have to be studied very carefully in order to get reproducible results. But even if the suspensions are reproducible, Beer's law does not hold or holds only over a narrow range of concentrations (scattering of light; see p. 688).

Reactions in colorimetry and spectrophotometry.

In colorimetry the constituent to be determined must usually be transformed into a colored compound. In general it is preferable to use those reactions in which the colored substance remains in true solution. If the reaction is reversible, the conditions should be arranged so that it goes virtually to completion, although this is not strictly necessary. If the reaction between the substance to be determined S, the reagent R, and the colored product C (in true solution) is represented by the equation

$$S + n\,R \rightleftarrows C,$$

the following relation holds under equilibrium conditions

$$\frac{[C]}{[S][R]^n} = K.$$

As a rule the excess of reagent is so great that $[R]^n$ can be considered constant. Therefore

$$\frac{[C]}{[S]} = K'$$

and Beer's law holds if there are no other complications. This is no longer true if C is not in true solution but in the suspended state.

The value of K or K' may vary with the temperature. If the comparisons are made with standards prepared under identical conditions, the temperature effect need not be considered. If, on the other hand, comparisons are made with permanent color standards or if the concentration is calculated from the measured intensity of the transmitted light (as with the spectrophotometer and gradation photometer), the effect of temperature must be known.

It is desirable to select only those reactions whose velocity is great and which therefore reach equilibrium in a very short time. In addition the colored reaction product should be stable, should not be light-sensitive, and should possess a reasonably intense color. In all cases the effect of foreign substances in the unknown solution should be considered.

Colorimetric methods and apparatus.

For an extensive discussion of the various types of colorimeters and special apparatus used in colorimetry, the student is referred to *Photometric Chemical Analysis*, by J. H. Yoe.[1]

In colorimetry the color of the unknown is generally compared with that of one or more standards of known concentration. With the spectrophotometer and the gradation photometer it is not necessary to prepare standards, since the concentration of the colored component in the unknown can be calculated from the absorption coefficient, the latter being experimentally determined.

The most common methods used in colorimetry in matching colors are the following:

1. *Standard series method* (equiconcentration of colored substance in unknown and standard).
2. *Balancing method* (the unknown and the standard are equicolored when viewed vertically through the lengths of the columns of the liquids).
3. *Absolute colorimetry* with gray solutions.

1. *Standard series method.* In this method the sample solution is made up to a definite volume, and the color is compared with that of a series of standards prepared in a similar way. The comparison is made in suitable glass vessels filled with unknown and standard to the same height and viewed vertically through the length of the column of liquid. The concentration of the unknown is equal to that of the standard having the same color. As a rule it will be found that the color intensity of the unknown lies between that of two successive standards. In such a case the concentration of the unknown is between that of the two standards and can be approximated if the concentrations in the two standards do not differ too widely. Usually it is best first to make a rough approximation of the concentration by taking standards of widely different concentrations. Then a set of standards is prepared of which the extremes are slightly lighter and darker, respectively, than the unknown, and two successive standards found, one of which is slightly more and the other less intense than the unknown. Suppose, for example, that the ammonia content of a water is to be determined by Nessler's method. A series of standards is prepared containing 0.05, 0.1, 0.2, 0.4, 0.6, and 0.8 mg. of ammonia per liter. Suppose that the color of the unknown is found to lie between that of the 0.2 and 0.4 mg. standards and closer to 0.2 than to 0.4 mg. A new set of standards is then prepared containing 0.2, 0.25, 0.3, and 0.35 mg. of ammonia per liter; and it is found that the unknown lies between 0.25 and 0.30 mg. per liter. The ammonia content of the unknown is then taken to be equal to 0.275 or 0.28 mg. per liter. This approximation is usually sufficient for ordinary purposes. If a more accurate approximation is desired, a standard of 0.275 mg. ammonia per liter is prepared and the unknown compared with the 0.25, 0.275, and 0.30 mg. samples. In approximate work, comparisons can be made in bottles of uniform size and shape, preferably with flat and parallel sides. The unknown and the standards are made up to the same volume and viewed against a background of white paper or of white frosted or opal glass. Equal and uniform illumination of the bottles is essential. The colorimetric determination of the pH of a solution is often made in test tubes of equal diameter. The tubes are placed in a wooden rack and rest on a perforated bottom. A white opal glass reflector is set at an angle below the rack so as to reflect light up through the tubes (Fig. 118a). More accurate results are obtained by the use of *Nessler tubes*.

---

[1] Volume I, *Colorimetry;* Volume II, *Nephelometry;* John Wiley and Sons, New York, 1928; for a review of photoelectric methods, see R. H. Müller, Ind. Eng. Chem., Anal. Ed. *11*, 1 (1939); of spectrophotometric methods, S. E. Q. Ashley, *ibid.* *11*, 72 (1939).

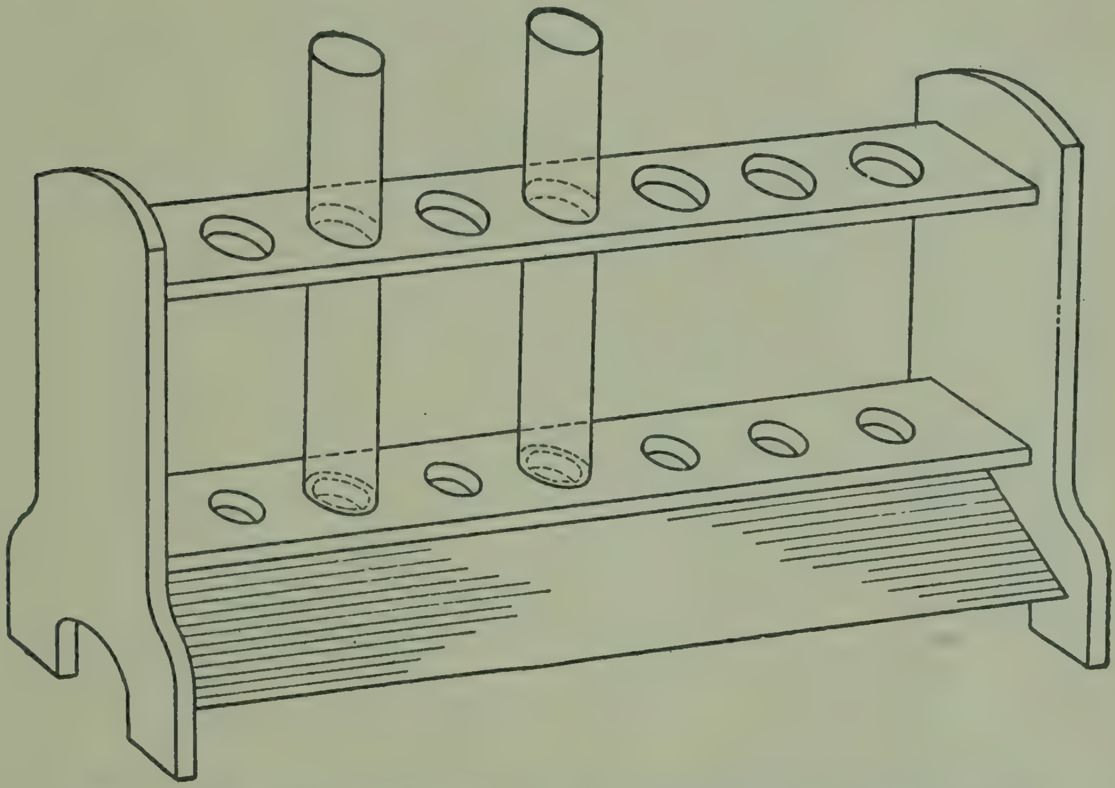


FIG. 118a. Tubes and rack for colorimetric comparisons.

These tubes must be made of clear glass, uniform in bore, and have polished flat bottoms. Two sizes are in common use, viz., tubes of 50 ml. and 100 ml. capacity. According to the specifications of the American Public Health Association, the 50 ml. mark on the 50 ml. tubes should be about 210 mm. from the bottom. In a set of tubes, the marks must be at the same height, or must not differ by more than 6 mm. The 100 ml. tubes may also be marked at 50 ml. In color matching, the Nessler tubes may be placed in a wooden box so arranged that the light is reflected from the bottom up through the tubes, the latter resting on a rack having a false bottom. The box should be painted a dull black inside.

100
ml
50
ml
50

FIG. 118b. Nessler tubes.

In some cases it is possible to avoid the preparation of a set of standards and to use permanent color standards for comparison. Permanent color standards of widely different colors can be obtained by mixing solutions of ferric chloride in dilute hydrochloric acid (yellow), cobalt chloride (pink), copper sulfate (blue), and potassium dichromate (orange).[1] Naturally the set of permanent color standards should be standardized against known amounts of the substance being determined, the latter always being treated under exactly identical conditions. In the last few years the use of series of colored glasses as standards has become popular. In using permanent color standards, great care must be taken that the *tint* (hue) of the color exactly matches that of the test solution.

Colorimetric titration. The principle and the practical performance of a colorimetric titration are extremely simple, but its field of application is limited. A known volume, say 100 ml., of the solution is measured out and transferred to a 150 ml. beaker or a bottle. A measured volume of reagent (or reagents) is then added. In another beaker or bottle of the same dimensions, 100 ml. of water and the same volume of reagent are placed. A solution containing a known concentration of the substance being determined is added to the blank solution from a micro-buret until the colors of the two samples match. If the volume of the standard solution required to match the color of the unknown is less than about 10 per cent of the total volume, the volume change due to the introduction of the solution may, as a rule, be neglected; otherwise, it may be allowed for by a simple calculation, or the determination may be repeated by taking $(100 - x)$ ml. of water, x being the volume of standard solution used in the first approximation.

Figure 119 shows the simple equipment recommended by Schoorl [2] and Karsten [3] for the performance of a colorimetric titration. The colorimetric cylinders should contain the same volume, be of the same diameter, and have flat bottoms. The tubes furnished by Schott and Gen. (Jena) satisfy the requirements. During the measurements, the tubes are placed in black paper cylinders to exclude extraneous light from the sides. They are placed on a thin colorless glass plate, which is put on the top of the little case. *A* is a stiff piece of white cardboard which can be adjusted to obtain the optimum illumination. It is of great importance to distribute the small amount of standard liquid added from the buret as quickly as possible throughout the entire liquid. For this purpose a stirring rod is used, the lower end of which is flattened to a width of about 1 cm.[1]

---

[1] Compare H. V. Arny and C. H. Ring, J. Franklin Inst. *180*, 199 (1915); J. Ind. Eng. Chem. 8, 309 (1916); H. V. Arny and A. Taub, J. Am. Pharm. Assoc. *12*, 839 (1923); A. Taub, *ibid.* *16*, 116 (1917); on the light absorption of mixtures of colored inorganic salt solutions, see J. P. Mehlig and M. G. Mellon, J. Phys. Chem. *35*, 3397 (1931); also J. Phys. Chem. *33*, 963 (1929); Mellon and C. T. Kasline, Ind. Eng. Chem., Anal. Ed. 7, 187 (1935); 8, 463 (1936).

[2] N. Schoorl, Chem. Weekbl. *27*, 52 (1930); *Commentaar op de Nederl. Pharmacopee*, I, p. 197.

[3] P. Karsten, *Bydrage tot de Colorimetrie*, Thesis, Groningen (Holland), 1934.

This method can be applied only when the color obtained is independent of the manner of mixing (in one vessel a very dilute solution of the substance to be determined is mixed with the reagent; in the other vessel a fairly concentrated solution of the substance to be determined is mixed with a dilute solution of the reagent). Also the color development should be virtually instantaneous, and, as in all other colorimetric determinations, foreign substances present in the unknown should not interfere with the color.

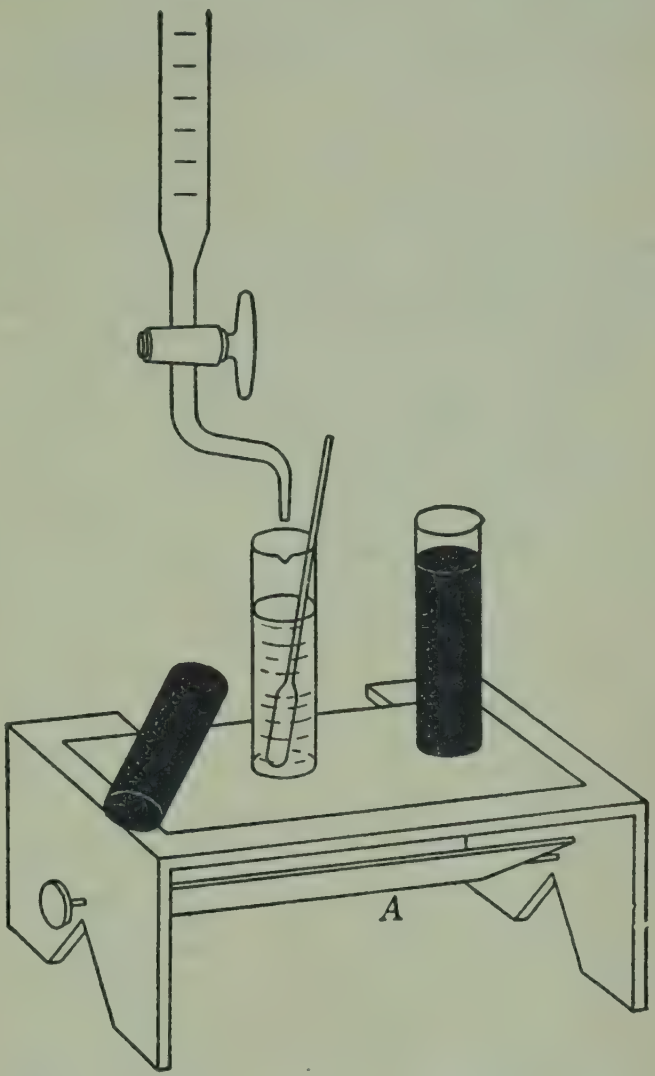


FIG. 119. Arrangement for colorimetric titration.

Under proper conditions the colorimetric titration method can be applied to the simple determination of lead in water with sodium sulfide or of ferric iron with thiocyanate.

A combination of the colorimetric titration method with a permanent color standard was made by Winkler[2] in the determination of silica in water. The silica is transformed by hydrochloric acid and ammonium molybdate into the strongly colored yellow silicomolybdate complex. A solution of the latter has the same color as a potassium chromate solution. Therefore, after transforming the silica in the sample into the yellow complex, an equal volume of water is taken in an identical container, and potassium chromate solution is added from a buret until the colors match. The chromate solution is standardized against solutions containing known amounts of silica.

2. ***Balancing method. Colorimeters.*** In the balancing method the color of the standard may be lighter or darker than that of the unknown. The comparison is made in tubes, but the height of one or both columns can be varied until the color intensities are the same when viewed through the lengths of the columns of the liquids. When the instrument is perfect and Beer's law is obeyed, the following relation holds at equal color intensity (see p. 648):

---

[1] See G. Lockermann, W. Ulrich, and T. Kunzmann, Chem. Ztg. *57*, 19 (1933).

[2] L. W. Winkler, Z. angew. Chem. *27*, 511 (1914).

$$R_x C_x = R_s C_s$$

and

$$C_x = \frac{R_s}{R_x} C_s.$$

R_s denotes the reading of the standard, and R_x that of the unknown as equal color intensity; C_s is the concentration of the substance in the standard, and C_x the concentration in the unknown. The equation is based on the simple rule that in those cases in which Beer's law holds, the concentrations of two colored solutions are inversely proportional to the thicknesses of the layers when the color intensities are the same. If the instrument used is not perfect or if Beer's law does not hold, the instrument must be calibrated in an empirical way.

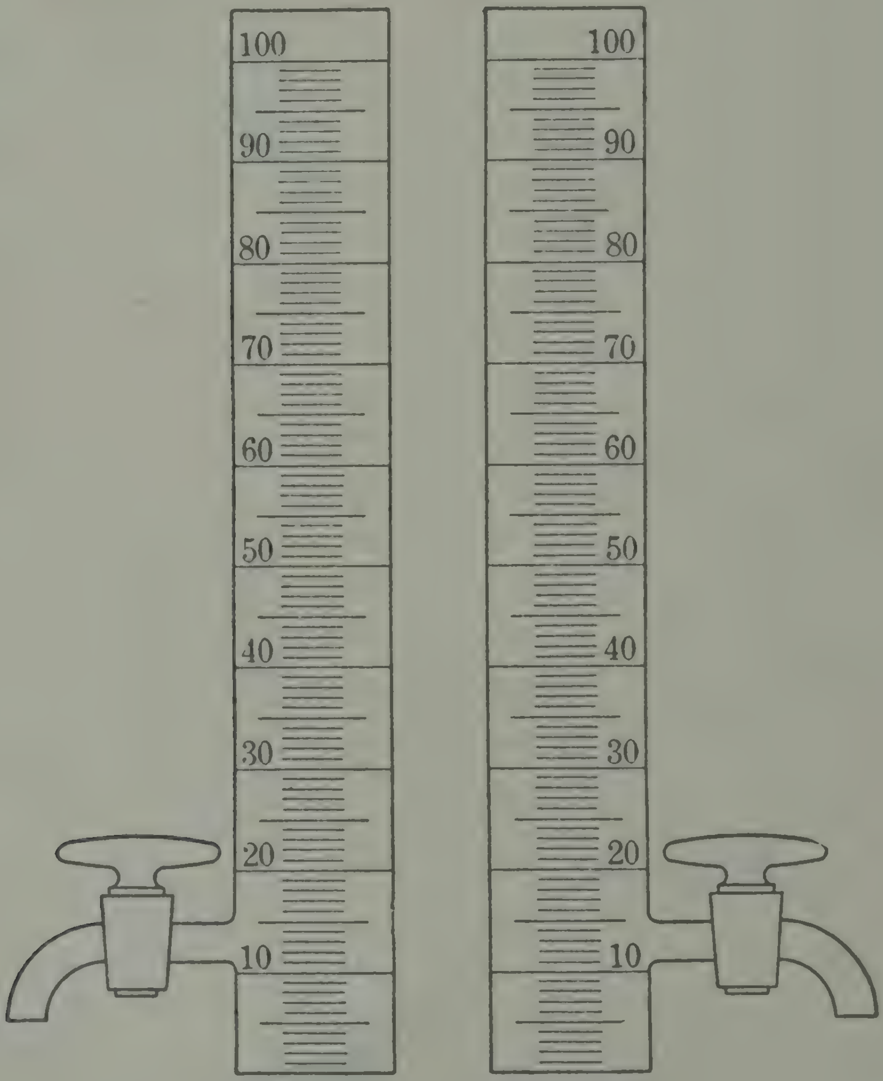


FIG. 120. Hehner cylinders.

A simple application of the above principle was made by Hehner,[1] who recommended graduated cylinders, with an outlet at the bottom. for colorimetric work. Hehner cylinders are used in pairs and are very useful in colorimetric work. Each cylinder has a glass stopcock about 2.5 cm. from the bottom, through which liquid may be drawn off until the color in the two cylinders is the same when viewed vertically. The cylinders should have flat, carefully ground, and polished bottoms of clear glass and should be uniform in bore.

---

[1] O. Hehner, J. Chem. Soc. *30*, 326 (1876).

They are graduated at 1 ml. intervals and usually have a capacity of 100 ml. The cylinders may be placed in a box so arranged that the light is reflected from the bottom of the latter up through the tube. The box should be painted a dull black inside. In this way a Hehner colorimeter is obtained. Most analytical laboratories nowadays are equipped with a modern colorimeter of the Duboscq type, one of which is described below [1] and illustrated schematically in Figure 121.

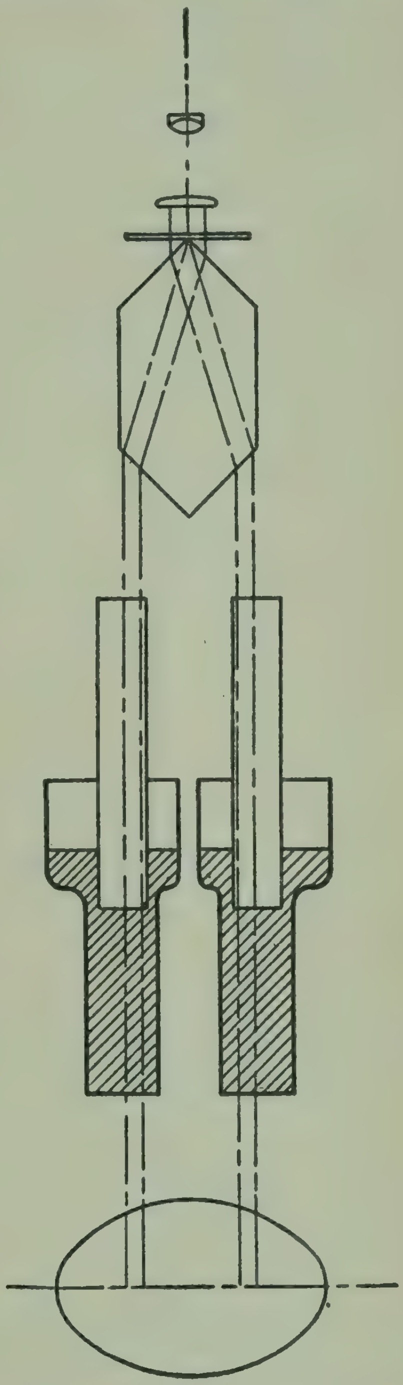


FIG. 121. Principle of the Duboscq colorimeter.

> "The rays which should be derived from a uniform source of light are reflected through two openings in the base of the apparatus, a plane mirror being used in the case of daylight, and a filament lamp with opal glass bulb in conjunction with a ground glass plate in the case of artificial light. The two pencils so admitted traverse two identically similar cups and plungers placed 25 mm. apart, and are then made to approach one another in passing through the symmetrical Albrecht-Hüfner glass body, so that in the field of view they appear separated by a very fine line. When the observer focuses the Ramsden eyepiece above the glass body upon its upper edge he sees the field of view divided into two semicircular half-fields. Of these the one on the right is uniformly filled with the light supplied by the left pencil, whilst the field under the left eye is lit up by the right pencil. The two fields, being thus separated by an extremely fine line, can be compared with ease and accuracy. It is imperative, if an exact reading is to result, that the illumination should be absolutely identical on both sides. It is to be noted that any soiled patches on the plane mirror or the opal plate cannot fail to vitiate this condition.
>
> "The cups which serve to receive the solutions are mounted movably on slides. They are in their proper central position when they meet the limit stops at the rear. The plungers by means of which the color identity is established in the half-field can be displaced with the aid of rack and pinion motions, by means of which the required depth of strata can be set to a nicety."

---

[1] For a description of a great variety of colorimeters, cf. J. H. Yoe, *loc. cit.*, especially p. 42; the quotation is taken from Yoe's book.

The cups are shielded from adventitious light by a black shield or more commonly by using black glass for the side walls. The depths of the strata which result from the descent and ascent of the plungers can be read off accurately to 0.1 mm. by means of the scales and verniers above the milled heads.

After taking the readings, the cups (and plungers) should at once be removed and cleaned. They should then be replaced and the colorimeter placed in the case.

Use of the colorimeter. Owing to optical and mechanical imperfections of most colorimeters, one usually does not get the same reading when the cups are filled with the same colored solution and balanced. For this reason one of the cups (say L) is filled with a solution of the same color and approximately the same intensity as the unknown (say the standard solution) and always used as a reference. The plunger is set at a certain reading somewhere near the middle of the scale and left unchanged during the subsequent manipulations. Before using the other cup, one should always make sure that the reading is zero when the plunger touches the bottom of the cup. If this requirement is fulfilled the cup is cleaned, rinsed, and filled with an appropriate standard solution having a color corresponding to a known concentration of the substance to be determined.[1]

The cup containing the standard solution (say R) is raised or lowered until equal color intensity is obtained in the two fields or, in other words, until the system is balanced. The cup should not be moved repeatedly about the balancing point but should be raised or lowered until the colors appear the same. The reading is taken and the balancing repeated five or ten times, in such a way that the balancing point is approached five times from the higher and five times from the lower side.[2]

The average of all the readings is obtained ($= S$). The cup is then removed, rinsed, and filled with the unknown, and the balancing repeated in the same way as described for the standard; and the average (U) is found.

Calculation. If Beer's law holds, the concentration x of the unknown is readily found from the following equation:

$$x = \frac{S}{U} C$$

in which C denotes the concentration of the substance in the standard solution. It should be noticed that the exact concentration and the composition of the *reference* solution are immaterial as long as it has the same color as the unknown and the standard.

---

[1] If the substance to be determined is colored, a solution of known concentration may be used as a standard. If the unknown is transformed into a colored compound, the standard is prepared with a known amount of the substance, using the same amounts of reagents in the same final volume and treated exactly as the unknown. In certain cases permanent color standards (see p. 654) can be used (e.g., potassium chromate in the silica determination, see p. 672).

[2] This procedure has been found to give the most satisfactory results since it reduces eye fatigue. Eye fatigue is generally one of the most important factors responsible for irreproducible readings. The operator should avoid looking at any bright light and should allow his eye to rest between successive sets of readings. If the operator feels eye strain, he should defer further readings until the eye recovers.

Illustration: The concentration of a dye solution was to be determined. The right cup was filled with a dye solution of about the same color intensity as the unknown and set at 25.0 (scale of colorimeter extended from 0 to 50 divisions), where it remained during the comparison. A standard solution, whose concentration was known to be 60 mg. of dye per liter, was placed in the left cup; and ten readings were taken as described. Then the left cup was rinsed and filled with the unknown, and ten readings were again taken. The following readings were obtained:

Standard (60 mg./l.)	Unknown (x mg./l.)
20.0	22.3
19.6	22.6
19.8	22.3
20.0	22.0
19.7	22.2
20.2	22.9
19.8	22.2
20.2	22.6
20.0	22.0
20.0	22.4
$S = 19.93$ or 19.9	$U = 22.35$ or 22.4

$$x = \frac{19.9}{22.4} \times 60 = 53.3 \text{ mg./l.}$$

If Beer's law does not hold, it is safest to arrange matters so that the color intensity of the standard lies within 10 per cent of that of the unknown. In routine work it is often preferable to construct a calibration curve, which may be done by changing the concentration of the standard while leaving the reference solution unchanged. The readings are plotted against the corresponding concentrations and a smooth curve drawn through the points. From the reading obtained with the unknown against the same reference, the concentration of the former is found from the curve.[1]

3. ***Absolute colorimetry with gray (neutral color) solutions.*** The principle of this method, which is strongly advocated by Thiel,[2] is the following: Monochromatic light passes, on the one hand, through one cup of the colorimeter containing a solution the specific extinction of which (see p. 647) is to be measured and, on the other hand, through the second cup containing a solution which absorbs the same constant fraction of light at the various wave lengths of the visible spectrum. If I_0 is the intensity of the incident light and I_t that of the transmitted light, we have

---

[1] For details see J. H. Yoe, *Photometric Chemical Analysis*, Vol. I, p. 70.

[2] A. Thiel, Z. anal. Chem. *94*, 170 (1933); Sitz. Ber. der Ges. zur Beförderung Naturw. zu Marburg, *71*, 17 (1936); Ber. *68*, 1015 (1935); Thiel and A. Logemann, Biochrem Z. *284*, 347 (1936); Thiel and O. Peter, *ibid. 271*, 1 (1934); Thiel, *Absolutkolorimetrie*, de Gruyter and Co., Berlin, 1939. Cf., however, E. Goldberg, *Eders Jahrbuch d. Photographie*, p. 149 (1911); *Z. wissenschaftl. Photographie 10*, 244 (1912).

$$I_t = I_0 10^{-xd}$$

in which x is the extinction of the unknown and d the thickness of the layer. Therefore

$$x = \frac{1}{d} \log \frac{I_0}{I_t}.$$

If now the intensity I_t of the light which has traveled through a layer of the unknown of thickness d_u is equal to that which has passed through a layer d_c of the comparison solution, we have

$$I_t = I_0 10^{-xd_u} = I_0 10^{-kd_c}$$

or

$$x = k \frac{d_c}{d_u}$$

in which k is the specific extinction of the comparison solution. Thiel has prepared a solution consisting of a mixture of dyes which has a constant specific extinction of 0.5 at various wave lengths. Therefore

$$x = 0.5 \frac{d_c}{d_u}.$$

Thus, if d_u is taken equal to 0.5 cm., $x = d_c$

Again we know that there is a simple relation between x on the one hand and the molar extinction coefficient ϵ and the concentration C on the other:

$$x = \epsilon C.$$

If the molar extinction coefficient ϵ of the unknown has been determined previously at the particular wave length, we have

$$C = 0.5 \frac{d_c}{d_u} \cdot \frac{1}{\epsilon}.$$

It is seen that the principle of absolute colorimetry is simple and from a practical viewpoint very promising indeed. A special colorimeter built by E. Leitz (Wetzlar) is strongly recommended by Thiel. A disadvantage of the method is that the "gray solution" is not quite stable and does not have an extinction of exactly 0.5 at various wave lengths. However, when this solution is made more perfect, it may be expected that "absolute colorimetry" will be of great practical use.

Sources of error in colorimetry.

In the theoretical part of this chapter a detailed discussion of the deviations from Beer's law is given. At this place some sources of error which must be considered quite generally in ordinary colorimetric work will be discussed.

1. In most colorimetric work the measurements are made with the naked eye. The observer must take care to avoid fatigue and eye strain. After a certain number of observations have been made, the eye becomes fatigued and is no longer sensitive to slight differences in intensity or shade. It is advisable to make the measurements in a dark room to prevent eye fatigue as much as possible, and to allow the eye to rest at intervals. In addition readings can be made with both eyes alternately. Generally the sensitivity of the eye increases with practice. However, some persons are unable to judge certain colors accurately. An operator

should test himself thoroughly for each color by matching a standard against itself in several degrees of intensity. The subjective error due to the limited sensitivity or imperfections of the eye is eliminated by the use of colorimeters in which a photoelectric or photronic cell is substituted for the eye.

2. The intensity of the color to be measured should be neither too great nor too small, since the eye is not sensitive in these cases to slight changes in intensity. Between these two extremes there is a range of intensities in which the eye has a constant sensitivity for the same relative change in the intensity. In other words the eye cannot distinguish between two intensities I and $I + \Delta I$, if ΔI is less than a certain fraction of I. Colorimetric determinations should be made in the range in which $\frac{I}{\Delta I}$ is constant. The value of this quotient naturally differs for various individuals and also depends upon the experience acquired. In addition the quotient is different for different colors; in general the eye is more sensitive to slight changes in red than in blue. With photoelectric and photronic devices the same point has to be considered.

3. The errors arising from different optical distributions in the instrument are discussed at great length by Dehn.[1] By using the procedure outlined on page 658, the errors due to optical imperfections of the instrument are mainly eliminated.

4. In some procedures the intensity and the shade of the color depend more or less upon the time of standing after the addition of reagents (e.g., ammonia according to Nessler), the acidity of the solution (ferric iron with thiocyanate), exact concentration of reagents, or presence of foreign constituents in the unknown. Therefore each procedure should be tested for its applicability under various conditions.

5. If the unknown contains suspended material (turbid solutions), no accurate comparison with a clear standard is possible.

If the unknown is colored by foreign substances, the ordinary procedure yields erroneous results. If the solution is slightly colored, it is still possible to make a colorimetric determination provided that the interference by the colored substance is eliminated. This is done in a most simple way by a device originated by H. Walpole[2] and which can

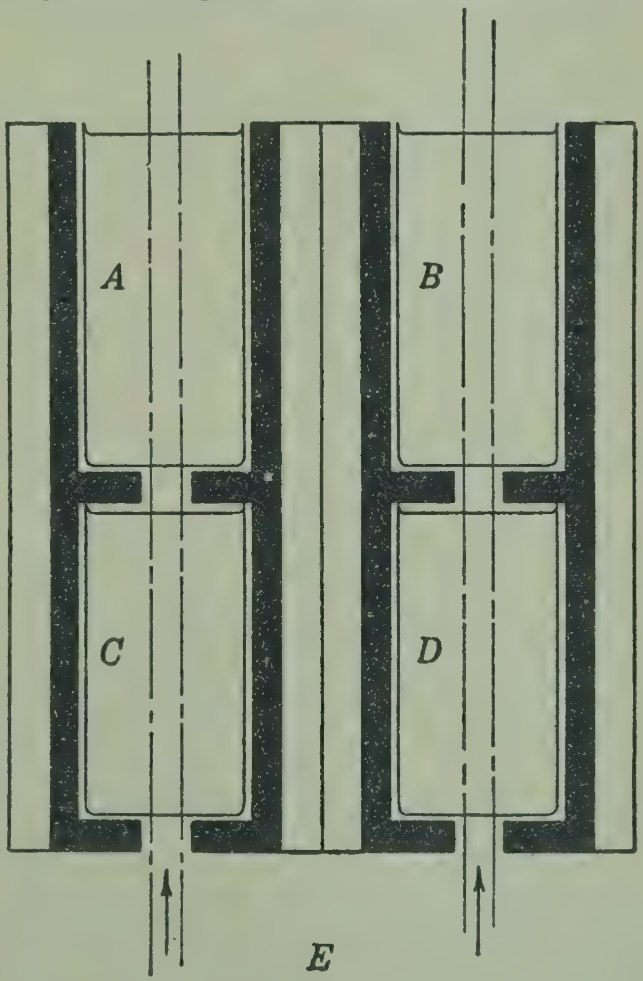


FIG. 122. The Walpole comparator.

---

[1] W. M. Dehn, J. Am. Chem. Soc. *39*, 1392 (1917).

[2] H. Walpole, Biochem. J. *5*, 207 (1911); *7*, 260 (1913); *8*, 628 (1914).

be applied to an ordinary colorimeter as well. The device is illustrated in Figure 122.

A, *B*, *C*, and *D* are glass cylinders with plane bottoms standing in a box which is painted a dull black on the inside. The mirror *E* provides a brightly illuminated background. *A* contains the colored solution to be tested with reagents. *C* contains an equal volume of water, and *D* the same volume of the originally colored unknown as has been added to *A*. Finally, *B* contains the solution of known strength for comparison. It is easily seen that by the above device the interference by the original color in the unknown is eliminated.

SPECTROPHOTOMETRY

A *spectrophotometer* is the combination of a *photometer* (a visual, photographic, or photoelectric instrument for measuring absolute or relative light intensities) with a *monochromator* (an instrument for isolating light of a single wave length). In some cases (photographic spectrophotometry) the monochromator actually is a spectograph.

The phrase "light of a single wave length" represents an idealization which cannot be attained. Depending in part upon the light source but mainly upon the dispersing apparatus, one may approach more or less closely to this ideal. Currently popular instruments use spectral bands ranging in width from 5 to 30 mμ.[1] A few elaborate photoelectric spectrophotometers at the present time use even narrower spectral bands, but they hardly come into consideration for ordinary analytical purposes. The combination of a photometer with light filters which transmit light in a narrow region of the spectrum is called an *abridged spectrophotometer* or *filter photometer*.

When a spectrophotometer or an abridged spectrophotometer is used. no comparisons need be made against solutions of known concentrations. With these instruments the intensity of the transmitted light or, better, the ratio $\frac{I_t}{I_o}$ is measured directly at a known thickness l. By changing l and c, the validity of the Lambert-Beer law (equation 10; constancy of ϵ) can be tested, and the value of the extinction coefficient ϵ can be determined. When ϵ is known, the concentration c_x of the unknown can be calculated simply from the relation (see equation 10):

$$c_x = \frac{\log I_o/I_t}{\epsilon l}.$$

It should be realized that the extinction coefficient depends upon the solvent used, the temperature, and the wave length of the incident light. With a suitable spectrophotometer, measurements can be made in the ultraviolet and infrared regions of the spectrum, where the colorimetric method is no longer applicable. In addition, the spectrophotometer has the following advantages:

1. It can be used in the analysis of a mixture of two colored components having absorption maxima at widely different wave lengths. If Beer's

---

[1] The range of the visible spectrum is approximately 400 to 700 mμ.

law holds and the extinction is an additive function of the concentrations of the two components, it is found that the *extinction exponent* κ_λ of the mixture at a certain wave length λ is equal to $(\kappa_1)_\lambda + (\kappa_2)_\lambda$, in which $(\kappa_1)_\lambda$ and $(\kappa_2)_\lambda$ denote the extinction exponents of the individual solutions with concentrations of c_1 and c_2 respectively.

$$\frac{I_t}{I_o} = 10^{-[(\kappa_1)_\lambda + (\kappa_2)_\lambda]} = 10^{-\kappa_\lambda} = 10^{-(\epsilon_1 c_1 + \epsilon_2 c_2)} \quad (l = \text{constant; equation 10})$$

since $$\epsilon_1 = \frac{(\kappa_1)_\lambda}{c_1} \quad \text{and} \quad \epsilon_2 = \frac{(\kappa_2)_\lambda}{c_2}.$$

Therefore $$\kappa_\lambda = (\kappa_1)_\lambda + (\kappa_2)_\lambda = \epsilon_1 c_1 + \epsilon_2 c_2. \tag{14}$$

ϵ_1 and ϵ_2 are known and κ_λ is determined. The measurements are made at two different wave lengths λ_1 and λ_2:

$$\kappa_{\lambda_1} = (\epsilon_1)_{\lambda_1} c_1 + (\epsilon_2)_{\lambda_1} c_2 \tag{15}$$

$$\kappa_{\lambda_2} = (\epsilon_1)_{\lambda_2} c_1 + (\epsilon_2)_{\lambda_2} c_2. \tag{16}$$

We now have two equations with two unknowns, c_1 and c_2, which are easily solved.

2. In most colorimetric determinations the dissolved substance to be determined is transformed into a colored compound. If the original solution has a color of its own, it will interfere with the colorimetric determination. In this case the determination can be made with a spectrophotometer. By measuring the extinction exponent κ of the original solution:

$$\frac{I_t}{I_o} = 10^{-\kappa_\lambda}$$

and of the solution after transforming the substance to be determined into the colored compound:

$$\frac{I_t}{I_o} = 10^{-(\kappa_\lambda + \epsilon_\lambda c_x l)},$$

the concentration c_x can be found if ϵ_λ has been determined previously. It is advantageous to work with light of a wave length such that the maximum absorption by the colored compound originally present in the solution is found at a wave length widely different from that of the colored compound whose concentration is to be determined.

A colored substance has an absorption spectrum in which the extinction coefficient varies with wave length (usually quite strongly). In spectral regions in which the substance is relatively transparent, the value ϵ is close to zero. If the transmission measurement is made with continuous white light (as in ordinary colorimetry), an average, over-all value of ϵ is used which is usually much smaller than the maximum value of ϵ at the peak of an absorption band. Therefore colorimetric methods cannot attain the concentration sensitivity of spectrophotometric methods.

Spectrophotometric methods and apparatus.

For a complete discussion of various types of spectrophotometers and appropriate procedures, the student is referred to any of the works listed below.[1]

The first investigator of absorption spectra was Brewster (1833) Apparently Vierordt (1873) [2] was the first to suggest that spectrophotometry provided a new and accurate method of chemical analysis. However, only in comparatively recent years has any considerable analytical use been made of spectrophotometry. Spectrophotometric work may involve visual, photographic, or photoelectric methods of measurement. Photographic methods have been, and are being, used very extensively in the determination of absorption spectra, especially in the infrared and ultraviolet regions; but they hardly come into consideration in ordinary quantitative inorganic analysis. Therefore only visual and photoelectric methods will be discussed.

Visual spectrophotometry

The most widely used visual spectrophotometers are constructed according to the following general scheme. Light from a continuous source (tungsten lamp) is sent through a monochromator.[3] A beam of the desired wave length and wave-length spread emerges from a suitable exit slit. The emergent monochromatic beam is divided into two parallel beams of equal intensity (see, e.g., arrangement in Fig. 121 on p. 657). The solution to be analyzed, contained in a suitable absorption cell, is placed in one of the beams; the solvent plus reagents, in an exactly similar cell, is placed in the other beam. Since the solution transmits less light than the pure solvent plus reagents, the two beams become of unequal intensity. The unequal beams are combined again so that each illuminates half of the field of view of an eyepiece (see p. 657). Some photometric procedure now is used to make the two beams of equal intensity. This ordinarily involves the use of polarizing prisms. The amount of light transmitted through two such prisms depends on their respective orientations, and it is possible by a suitable choice of prism positions to extinguish completely a beam of light. Since the amount of light transmitted through two such prisms varies in a known way with the relative orientation, this allows one to determine directly the relative intensities of the two beams.

Alternatively one may measure the relative intensities with a "neutral wedge." In its simplest form this consists of a wedge-shaped piece of black glass, the thickness being chosen so that it is nearly transparent at one end and nearly opaque at the other. Such a wedge may be calibrated by determining the percentage of light transmitted through various portions. It may then be inserted in the path of the more intense beam to reduce its intensity to match that of the weaker beam.

---

[1] W. Brode, *Chemical Spectroscopy*, John Wiley and Sons, New York, 2d ed., 1941.
F. Twyman and C. B. Allsopp, *The Practice of Absorption Spectrophotometry*, Adam Hilger, Ltd., London, 2d ed., 1934.
F. Weigert, *Optische Methoden in der Chemie*, Akad. Verlagsges., Leipzig, 1927.

[2] K. Vierordt, *Die Anwendung des Spektralapparates zur Photometrie der Absorptionsspectren und zur quantitativen chemischen Analyse*, H. Laupp, Tübigen, 1873.

[3] Usually this is a small one-prism instrument similar to an ordinary spectrometer. When results of the greatest accuracy are desired, a double monochromator is used, in which the second dispersion serves to reduce the amount of stray light (due to reflections from lens and prism surfaces, etc.). Stray light is an important limiting factor in obtaining accurate analytical results.

Photoelectric spectrophotometry.

The special advantages of photoelectric methods are (1) the elimination of the personal factor, which is of major importance in photometric work, and (2) extension of practical analysis to the red and blue ends of the spectrum, at which the sensitivity of the eye is extremely low.

Because of these advantages, photoelectric spectrophotometers, quite rare twenty years ago, are now in considerable use. The precision attainable by routine photoelectric work is about the same (a few per cent) as that in careful visual work. In especially favorable cases with attention paid to every source of error, it is possible to attain a precision of a few tenths of one per cent.

In photoelectric abridged spectrophotometry, the amount of light available even after absorption by the samples is sufficient to allow the use of an ordinary photronic cell with a microammeter or low-sensitivity galvanometer as the measuring instrument, no amplification being needed. In spectrophotometry (monochromator) only a very narrow band of the spectrum is used, and the amount of light available for measurement is extremely small. Therefore it is necessary to use a photoelectric cell with one or more stages of amplification. A great deal of the increase in popularity of photoelectric spectrophotometry in recent years may be traced to the remarkable development of the photo cells and of simple, stable amplifying circuits.

Methods.

The simplest method is that of substitution. The solution is placed either before or behind the slit of the monochromator. The current or voltage developed is measured. The measurement of potential is preferable since it eliminates the need of verifying linear response of the measuring system. The solvent is then placed in the same position as that previously occupied by the solution, and the current or potential is again measured. The ratio of the two results gives directly the percentage transmission. All photocells in common use give a response which is directly proportional to the light intensity, at the intensity levels used for these measurements. Use of the above principle is made in the Coleman photoelectric spectrophotometer (Fig. 123).

This simple and rapid method is subject to one major disadvantage. The light source must remain at constant intensity for the two measurements. Quite generally the accuracy of this method is determined by the stability of the light source.

There are two procedures which eliminate error due to instability of the light source. One method uses two photocells in a bridge arrangement, so that one measures the relative intensity directly (e.g., in Lange colorimeter). This method, however, has the disadvantage that it requires photocells which are identical in spectral response and sensitivity. Actually it is quite difficult to find two cells matched within sufficiently close limits.

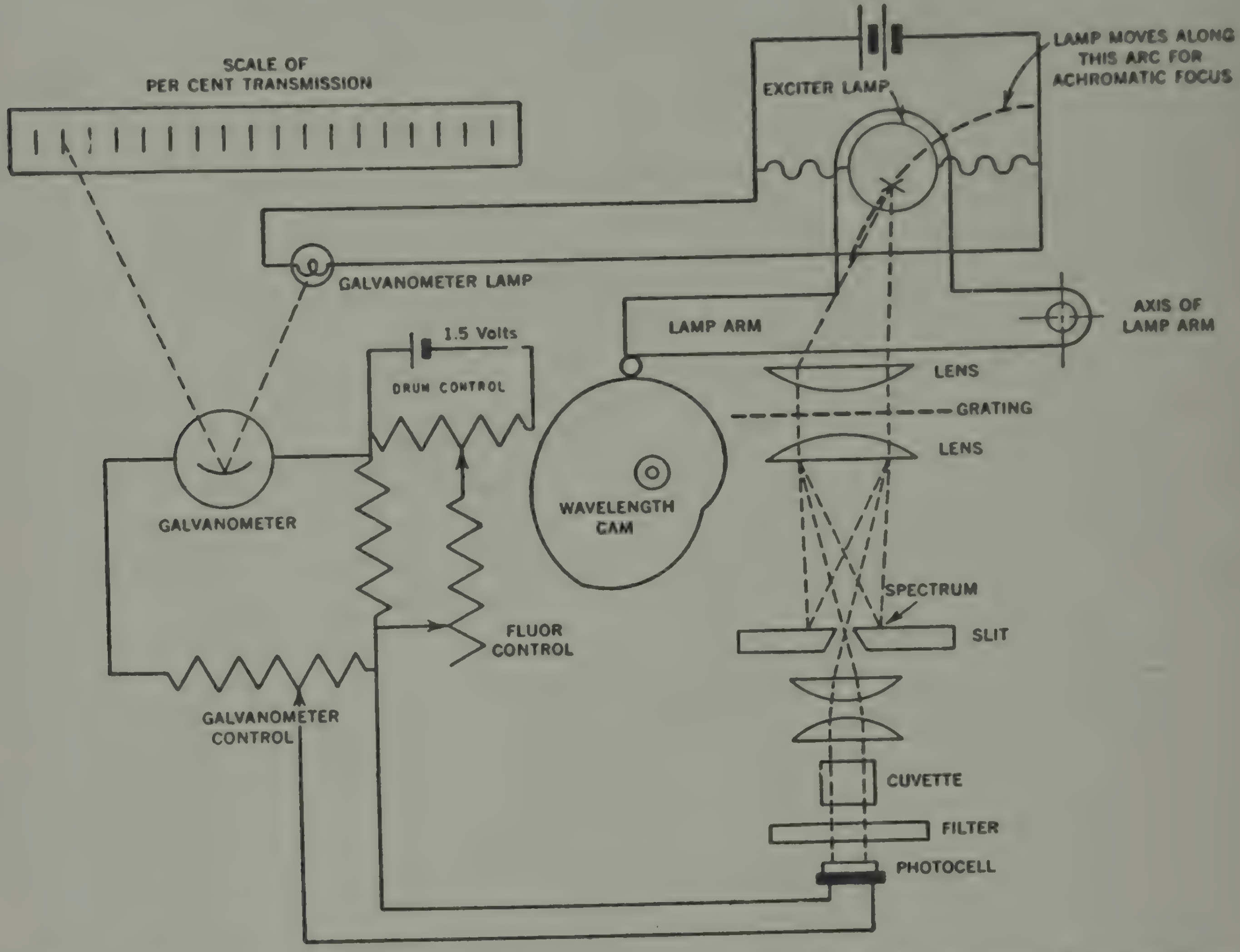

SCALE OF
PER CENT TRANSMISSION
EXCITER LAMP
LAMP MOVES ALONG THIS ARC FOR ACHROMATIC FOCUS
GALVANOMETER LAMP
1.5 Volts
DRUM CONTROL
LAMP ARM
AXIS OF LAMP ARM
LENS
GRATING
LENS
WAVELENGTH CAM
GALVANOMETER
SPECTRUM
SLIT
FLUOR CONTROL
GALVANOMETER CONTROL
CUVETTE
FILTER
PHOTOCELL

FIG. 123. Schematic diagram of Coleman Model 11 Universal Spectrophotometer. (Courtesy of Coleman Electric Co., Inc.)

The other procedure is best of all in principle and in practice but requires the most elaborate experimental arrangement. The beam of monochromatic light is divided into two equal beams. One beam passes through the solvent, the other through the solution; the beams are recombined and are brought to the photoelectric cell. The beams are not juxtaposed, as in the visual instrument, but illuminate the same part of the photosensitive surface. Now a suitable disk is rotated rapidly (for example, 2500 r.p.m.) in the path of the beam, so that it blocks off first one beam, then the other. This causes the intensity of illumination on the photocell to change periodically, just as rapidly as the disk is rotating. An alternating current is produced, the magnitude of which is determined by the relative light transmissions of solution and solvent. There are two ways of proceeding: (1) the alternating current itself is measured by using a suitable A. C. amplifier and galvanometer. This is quite rapid but has the disadvantage that measurements made at various periods of time will be comparable only if the sensitivity of the photocell remains constant. (2) The alternating current is not measured but is reduced to zero by suitable photometric balancing of the light beams, and the photometer reading itself determines the relative intensities. Evidently in this method it is immaterial whether the light source and the photocell sensitivity remain constant.[1]

Choice of wave length. It is important to avoid making measurements in a region where the extinction coefficient ϵ changes rapidly with the wave length, for a small error in setting the wave-length scale will result in a large change in the apparent extinction coefficient. Therefore, the wave length corresponding to the maximum of ϵ should be used. When the transmission of the solution increases continuously over the wave-length range covered by the light filter, Beer's law will be found not to be obeyed. This limitation does not exist in visual colorimetry.

Choice of concentration.

This is important in photoelectric spectrophotometry and colorimetry. For the sake of concreteness let us assume that photo current is the measured quantity. Therefore the limiting factor is the uncertainty in the galvanometer reading, dG. This applies only to the value of G corresponding to the transmission of the solution, for the uncertainty in the reading for the solvent (corresponding to I_o) obviously cannot be affected by the choice of concentration of unknown. We assume a steady light source and a linear relation between intensity and galvanometer deflection. Then

$$G = k \cdot I_t \quad \text{and} \quad dG = k \cdot dI_t$$

If Beer's law applies (we shall keep l constant),

$$I_t = I_o e^{-klc}$$

Put $\ln \frac{I_o}{I_t} = E$, the "extinction."

$$E = \ln I_o - \ln I_t = \ln I_o - \ln I_o e^{-E}$$

The accuracy of the determination is given by

$$\frac{dc}{c} = \frac{dE}{E} = - \frac{dI}{E \cdot e^{-E}},$$

which is a minimum when $E \cdot e^{-E}$ is a maximum. This occurs when $E = 1$ or $\log \frac{I_t}{I_o} = 0.4343$. This corresponds to 36.8 per cent transmission.

Hence, to get the most accurate results in photoelectric colorimetry and spectrophotometry, one must adjust c to give 36.8 per cent transmission.

---

[1] This principle is employed in an automatic recording instrument of the General Electric Company. The alternating current produced by the unequal intensities runs a motor which rotates a polarizing prism in the path of the stronger beam in such a way that the intensities are brought to equality. When the beams are of equal intensity, evidently the motor stops, and the reading of the rotation of the polarizing prism is recorded automatically.

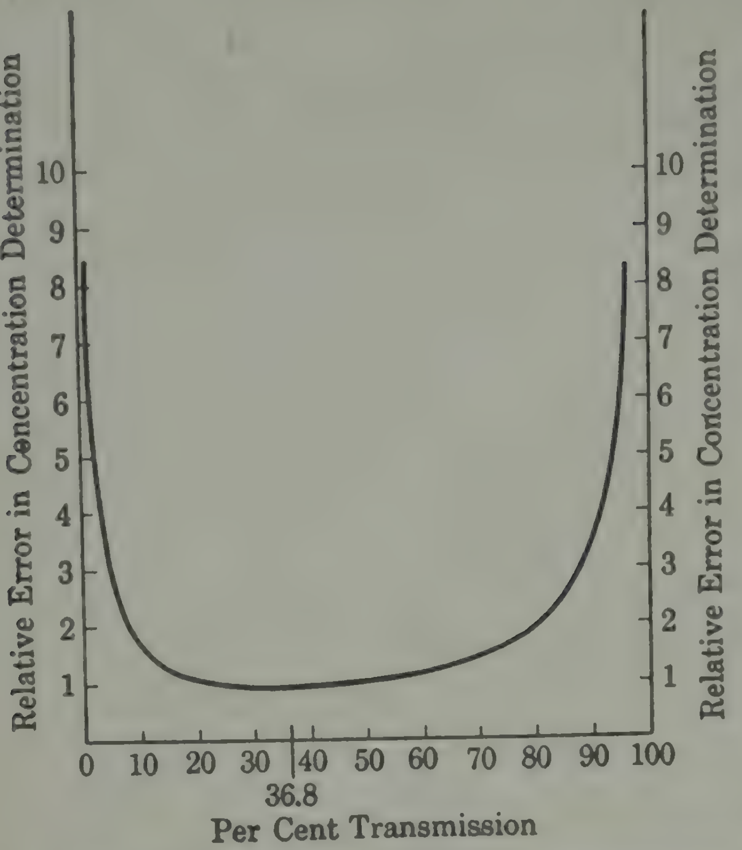


FIG. 124. Relative error in photoelectric photometry at different percentages transmission.

Actually by evaluating $E \cdot e^{-E}$ as a function of E, it is found that this value is not critical. If one has a galvanometer which can be read at full scale to ± 0.5 per cent, the maximum accuracy in a concentration determination will be 1.4 per cent. If the solution transmits 50 or 20 per cent, the error in c is 1.6 per cent. The actual variation is shown in Figure 124. Using the same galvanometer as above, we would find that a determination accurate to 2.0 per cent could be carried out within the range 13–70 per cent transmission. But beyond these limits the error increases very rapidly.

EXERCISES IN COLORIMETRY AND SPECTROPHOTOMETRY

Determination of ammonia by Nessler's reagent.

An alkaline solution of mercuric iodide in potassium iodide was first proposed as a reagent for the colorimetric determination of ammonia by Nessler[1] in 1856. Since that time several modifications of the reagent have been made. When an alkaline potassium mercuric iodide solution is added to an ammonium salt solution, the liberated ammonia reacts with the reagent to form an orange-brown product which remains in colloidal solution but flocculates on long standing. The colorimetric comparison must be made before flocculation occurs. However, it cannot be made immediately after addition of the reagent, since the development of the color of the reaction product, which, according to Nichols and Willits,[2] has the composition $NH_2Hg_2I_3$, does not occur instantaneously. According to Nichols and Willits the reaction between ammonia and the reagent takes place in the following steps:

$$\begin{array}{r}
2\,(HgI_2 \cdot 2\,KI) + 2\,NH_3 \rightarrow 2\,(NH_3HgI_2) + 2\,KI \\
2\,(NH_3HgI_2) \rightarrow NH_2Hg_2I_3 + NH_4I \\
\hline
2\,(HgI_2 \cdot 2\,KI) + 2\,NH_3 \rightarrow \underset{\textit{(red-brown)}}{NH_2Hg_2I_3} + 2\,KI + NH_4I
\end{array}$$

The ammonium iodide again reacts with more reagent to form $NH_2Hg_2I_3$.

The Nessler determination of ammonia finds many applications. It can be used directly for the determination of ammonia in highly dilute ammonium chloride solutions and in water. In the presence of interfering substances, the ammonia is first separated by distillation under the proper conditions. The method is also applied to the determination of nitrogen in small quantities of organic substances after destruction of the organic material and distillation of the ammonia (micro-Kjeldahl; see p. 565). Nitrates and nitrites in alkaline medium are reduced by Devarda metal, or other suitable alloys, to ammonia, which is distilled and determined according to Nessler. Thus the method is used for the determination of small amounts of nitrates and nitrites. The advantage of the method lies in the fact that it can be used for concentrations of ammonia as low as 0.1 mg. per liter. A disadvantage is that the colorimetric method gives results far less accurate than the volumetric method, and therefore it is usually applied only to the determination of micro quantities.

---

[1] J. Nessler, Chem. Zentralbl. *27*, N. F. I. 529 (1856).

[2] M. L. Nichols and C. O. Willits, J. Am. Chem. Soc. *56*, 769 (1934).

Determination of ammonia in dilute ammonium chloride solution.[1]

Apparatus: Standard Nessler tubes (see p. 653).

Reagents: (1) *Ammonia-free water* (see p. 170).

(2) *Nessler reagent.*[2] "Dissolve 50 g. of potassium iodide in a minimal volume (about 35 ml.) of cold ammonia-free water. Add a saturated solution of mercuric chloride until a slight precipitate persists. Add 400 ml. of 9 *N* potassium or sodium hydroxide clarified by sedimentation. Dilute to 1 liter, allow the solution to clarify and decant. This reagent should give the characteristic color with ammonia within five minutes after addition and should not produce a precipitate with small amounts of ammonia within two hours."

(3) *Standard ammonium chloride solution.* "Dissolve 3.82 g. of ammonium chloride in ammonia-free water and dilute to 1 liter; from this stock solution prepare the standard solution by diluting 10 ml. to 1 liter with ammonia-free water: 1 ml. contains 0.01 mg. of nitrogen, equivalent to 0.0129 mg. of NH_4."

Procedure. If necessary dilute the sample to give an ammonia concentration of about 1 mg. per liter, and fill a Nessler tube of 50 ml. to the mark. "Prepare a series of 16 Nessler tubes containing the following volumes of standard ammonium chloride solution diluted to 50 ml. with ammonia-free water: 0.0, 0.1, 0.3, 0.5, 0.7. 1.0, 1.4, 1.7, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, and 6.0 ml. The standards will contain 0.01 mg. of nitrogen for each 1 ml. of the standard solution."

Nesslerize the standards thus prepared and the unknown solution by adding 1 ml. of Nessler reagent to each tube. It is not necessary to stir the contents of the tube after adding the reagent since the latter, being very dense, sinks through the solution at once. Allow the tubes to stand ten minutes after addition of the reagent, and then compare the color produced in the unknown with that in the standard by looking down through the tubes at a white surface so placed in front of a window that the light is reflected upward (see p. 652). The color of the unknown should be more intense than that of the most dilute standard and less intense than that of the most concentrated standard. Express the result in mg. of nitrogen or mg. of ammonia per liter of the sample.

---

[1] Ordinary distilled water often contains enough ammonia to enable it to be used as a suitable sample.

[2] The material in quotation marks is taken from *Standard Methods for the Examination of Water and Sewage*, 7th ed., pp. 14 *et seq.*, American Public Health Association, New York, 1933.

NOTES:

1. Permanent standards prepared by mixing 0.2 per cent solution of potassium chloroplatinate (K_2PtCl_6) in 1.2 *N* hydrochloric acid and 1.2 per cent cobalt chloride ($CoCl_2 \cdot 6\ H_2O$) in 1.2 *N* hydrochloric acid in the right proportions can be used. (For directions see *Standard Methods of Water Analysis.*)

2. In the determination of ammonia nitrogen in potable water, the sample (slightly alkaline) is distilled, and the distillate is nesslerized. The distillation concentrates the ammonia and, moreover, eliminates calcium and magnesium, which interfere by giving precipitates with the Nessler reagent. The interference of the latter can be overcome by adding alkali tartrate to the water and then nesslerizing without distilling; the tartrate forms complexes with calcium and magnesium which are not precipitated in the alkaline solution. This method of direct nesslerization can be applied when the water is clear, colorless, and contains not too little ammonia.

Determination of ferric iron.

Traces of iron are usually determined colorimetrically with thiocyanate as reagent. Ferric iron reacts with thiocyanate to give an intensely red-colored compound which remains in true solution, whereas ferrous iron does not react. It is remarkable that the mechanism of the reaction between ferric iron and thiocyanate, which has been the subject of so many studies, is still incompletely known. In the following, we shall see that a great number of factors affect the color shades or the color intensity of the red compound formed, and the method is therefore far from ideal from an analytical viewpoint. However, with the proper procedure and with due consideration of possible interferences, satisfactory results are obtained.

It is often stated that the red color obtained on addition of thiocyanate to ferric iron is to be attributed to the formation of ferric thiocyanate, which is partly dissociated into ferric and thiocyanate ions:[1]

$$Fe^{+++} + 3\,CNS^- \rightleftarrows Fe(CNS)_3.$$

Schlesinger and Van Valkenburgh,[2] however, found that the red solution contains the complex $Fe(CNS)_6^{\equiv}$ and attributed the red color to the formation of $Fe[Fe(CNS)_6]$. This view is substantiated by the facts that the molecular weight of the red substance in ether or benzene corresponds to this formula and that upon electrolysis in aqueous medium the complex $Fe(CNS)_6^{\equiv}$ ion migrates to the anode. The total equilibrium is very complicated:

$$\underset{(red)}{Fe[Fe(CNS)_6]} \rightleftarrows Fe^{+++} + Fe(CNS)_6^{\equiv} \tag{1}$$

$$Fe(CNS)_6^{\equiv} \rightleftarrows Fe^{+++} + 6\,CNS^-. \tag{2}$$

---

[1] G. Magnanini, Z. physik. Chem. *8*, 1 (1891).

[2] H. I. Schlesinger and H. B. Van Valkenburgh, J. Am. Chem. Soc. *53*, 1212 (1931).

On the other hand, recent investigations[1] have shown that the red color is due to $FeCNS^{++}$:

$$Fe^{+++} + CNS^{-} \rightleftarrows FeCNS^{++}.$$

In the colorimetric determination of iron a large excess of thiocyanate is used, and the iron undoubtedly will be present in several forms.

Effect of concentration of thiocyanate upon the color. Considering equations (2) and (1), it is easily understood that the color intensity increases with increasing thiocyanate concentration. Therefore in the colorimetric determination of iron it is desirable to use a very large excess of reagent. Under these conditions Beer's law holds[2] over a fairly wide range of iron concentrations; in addition the color obtained is more stable than with small amounts of thiocyanate.

Influence of acid upon the color. Owing to strong hydrolysis, solutions of ferric salts in water contain relatively few ferric ions. Addition of a strong acid suppresses the hydrolysis and therefore intensifies the color obtained with thiocyanate. The effect of the acid depends upon its kind and its concentration. Karsten[3] found that with a large excess of thiocyanate the color is practically independent of the concentration of nitric or hydrochloric acid, if the acid normality in the mixture is between 0.05 and 0.5 N. Karsten prefers nitric acid to hydrochloric acid, since the color obtained with the former is more stable. Sulfuric acid should not be used because sulfate ions have a tendency to form complexes with ferric ions, and consequently above a certain acidity the color intensity decreases with increasing sulfuric acid concentration.

Interfering substances.

Cations. Cupric copper if present in quantities greater than 2 mg. per liter (Karsten, *loc. cit.*) interferes by formation of a light-green coloration with thiocyanate. Mercuric mercury forms slightly dissociated $Hg(CNS)_2$ and complex $Hg(CNS)_4^{=}$ ions with an excess of thiocyanate. It therefore removes some of the reagent and gives a lighter color. By using a large excess of thiocyanate, the interference is hardly noticeable with relatively small amounts of mercury (less than 1 g. per liter). Bismuth in quantities greater than 100 mg. per liter may give rise to the formation of complex bismuth thiocyanate ions with a yellow color. Zinc and cadmium in larger quantities interfere. Nickel and cobalt and large amounts of manganese give colored complexes with thiocyanate.

Anions. Phosphates, fluorides, and oxalates interfere even in small quantities since they form fairly stable complexes with ferric ions. The interference by sulfates is less strong but still very pronounced. Nitrates and chlorides have a slight effect when present in large amounts, nitrates less than chlorides.

From the above it is evident that one must be careful in the application of the colorimetric iron determination with thiocyanate in solutions containing unknown amounts of salts. The following procedure can be used without any special precautions in the determination of iron in drinking water, which as a rule is poor in salts. In other cases, when indeterminate amounts of salts are present, it is advisable to precipitate the iron with a slight excess of ammonia, dissolve the washed hydrous iron oxide in dilute acid, and determine the iron in the solution so obtained.

---

[1] H. E. Bent and C. L. French, J. Am. Chem. Soc. *63*, 568 (1941).

[2] For a spectrophotometric study see J. T. Woods and M. G. Mellon, Ind. Eng. Chem., Anal. Ed. *13*, 551 (1941).

[3] P. Karsten, *Bijdrage tot de Colorimetrie*, Thesis, Groningen (Holland), 1934.

Standard iron solution. Prepare a solution of ferric chloride or ferric ammonium sulfate containing about 1 g. of iron and 10 ml. of concentrated hydrochloric acid per liter. Determine the iron content (see p. 320) and prepare a standard in 0.5 N hydrochloric acid containing 100 mg. of iron per liter.

Procedure. Add to 50 ml. of solution in a colorimeter glass (see p. 654) 5 ml. of 3 N potassium thiocyanate and 1 to 5 ml. 4 N hydrochloric or nitric acid. Add the same amounts of reagents to 50 ml. of water, and add standard iron solution from a buret until the colors are equal. The best results are obtained at iron concentrations between 0.04 and 0.1 mg. iron per 50 ml. of solution.

NOTES:

1. The standard and unknown should be compared immediately after preparation, since the colors fade on standing. This effect is caused by a reduction of the ferric iron by thiocyanic acid.

2. The determination can also be made with a colorimeter or with Nessler tubes.

3. If iron present in the ferrous state is to be determined, it is easily oxidized by adding a little bromine water to the solution. The excess of bromine need not be removed as it is reduced immediately by the thiocyanate.

Silica.

Dissolved silica reacts with molybdate in mineral acid medium to form an intensely yellow-colored heteropoly acid $H_8[Si_2(Mo_2O_7)_6]$. The color of this complex is similar to that of potassium chromate solutions; the latter therefore can be used for preparing permanent standards for the colorimetric silica determination. Phosphates and arsenate also react with molybdate in acid medium to give the yellow heteropoly acids $H_7[P_2(Mo_2O_7)_6]$ and $H_7[As_2(Mo_2O_7)_6]$.

The reaction between silicate, molybdate, and acid is not instantaneous, the time required for the development of the maximum color depending upon the concentration of molybdate and the concentration and kind of mineral acid used. After development of the maximum color, the latter fades slowly.

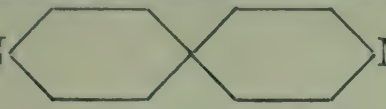
The colorimetric silica determination with molybdate and acid originated with Jolles and Neurath.[1] In 1914 Winkler[2] gave a very simple procedure which is used quite generally[3] and is described below.

---

[1] A. Jolles and F. Neurath, Z. angew. Chem. *11*, 315 (1898).

[2] L. W. Winkler, Z. angew. Chem. *27*, 511 (1914).

[3] For a more complete bibliography compare M. C. Schwartz, Ind. Eng. Chem., Anal. Ed. *6*, 364 (1934).

The oxidation potential of acid molybdate solutions is greatly increased by complex formation with silicate, phosphate, or arsenate. Thus it was found by Feigl [1] that an acid molybdate solution is not reduced by the weak organic base benzidine, H_2NNH_2, whereas the yellow heteropoly acids are reduced instantaneously to molybdenum blue. In addition the benzidine is oxidized to benzidine blue, which has an intense color. The reaction is extremely sensitive and is used for the detection and colorimetric determination of traces of dissolved silica, phosphate, and arsenate. For the detection of small amounts of silica in the presence of about 250 times as much phosphate or less, Feigl makes use of the fact that the yellow phosphomolybdate complex is decomposed by oxalic acid, whereas the silico complex is not affected. Therefore, before adding the benzidine, some 1 per cent oxalic acid solution is added, which makes the phosphate harmless. Instead of benzidine, stannous chloride is often used.[2] The latter gives a more stable blue solution.

Determination of silica in natural water.[3]

Reagent: *Ammonium molybdate.* 30 g. of ammonium molybdate, 200 ml. of 1 : 1 hydrochloric acid, 400 ml. of water.

Standard solution: 0.530 g. *potassium chromate* (K_2CrO_4) in 100 ml. water.[4] One ml. of this solution is equivalent to 1 mg. of SiO_2.

Procedure. Measure 50 ml. of the sample into a tall-form Nessler tube, and add 5 ml. of the molybdate reagent. Shake thoroughly and allow to stand for about fifteen minutes (not longer than twenty minutes). Add standard chromate solution from a buret to 50–55 ml. of distilled water in a Nessler tube until the color matches that of the unknown. 1 ml. of standard solution corresponds to 20 mg. of SiO_2 *per liter* of the sample.

NOTES:

1. Instead of using Nessler tubes, suitable beakers can be employed and the color comparison made as described under "colorimetric titration" (p. 654). Measure 100 ml. of the sample into the beaker, add 10 ml. of molybdate reagent, and proceed further as described above. In this case 1 ml. of standard solution corresponds to 10 mg. of SiO_2 per liter of the sample.

2. Suspended silica is not determined by the above procedure. Phosphate behaves qualitatively as silicate, one ml. of the standard being equivalent to approximately 2 mg. of P_2O_5. Reducing substances, such as hydrogen sulfide and ferrous iron, interfere because they give a blue color; they must be removed. Ferric iron interferes if present in quantities larger than 2 mg. per liter.

Use of the Duboscq colorimeter.

Determination of manganese in steel. For procedure see page 713.

Determination of titanium in a rock. For procedure see page 742.

---

[1] F. Feigl, Z. anal. Chem. *61*, 454 (1922); *74*, 386 (1928); *77*, 299 (1929).

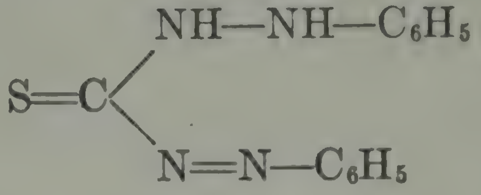
[2] See, e.g., R. J. Robinson and H. E. Wirth, Ind. Eng. Chem., Anal. Ed. 7, 147 (1935).

[3] See *Standard Methods of Water Analysis*, 7th ed., p. 66.

[4] H. W. Swank and M. G. Mellon, Ind. Eng. Chem., Anal. Ed. *6*, 348 (1934), recommend the use of a buffered chromate solution. They add the standard to 50 ml. of a 0.5 per cent borax solution instead of to 50 ml. water.

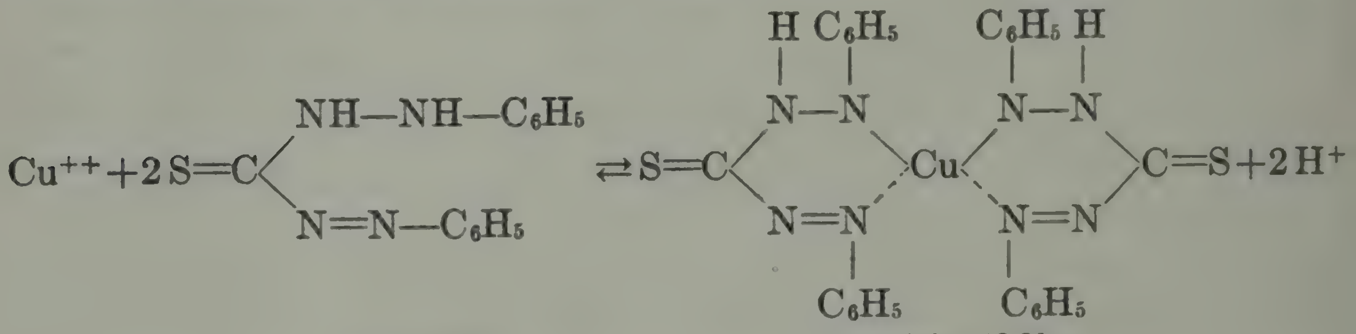
Use of the photoelectric photometer.

Determination of copper with dithizone. Diphenylthiocarbazone, or dithizone,



is a reagent which finds widespread use in the colorimetric determination of traces of many heavy metals.[1] When a solution of dithizone in carbon tetrachloride or chloroform (green) is shaken with an aqueous solution of a reacting metal having the proper pH, the strongly colored metal dithizonate is formed and dissolves in the organic solvent; the latter becomes red, violet, or yellow, depending upon the particular metal. Both dithizone and the dithizonates are insoluble in acid aqueous solutions. Dithizone is soluble in alkaline solutions (yellow color).

Silver, palladium, gold, mercury (I and II), and copper react with dithizone in mineral acid solution. The reaction



green (CCl_4) violet (CCl_4)

proceeds quantitatively to the right if the acidity is not too high (0.1 *N* or less) and a slight excess of dithizone is present. The mass-action law applies:[2]

$$\frac{[CuDz_2]_{CCl_4}}{[Cu^{++}]_{H_2O}} = K\,\frac{[HDz]^2_{CCl_4}}{[H^+]^2_{H_2O}}$$

Metals such as lead, zinc, nickel, and cobalt do not react appreciably in acid solution but will react completely with dithizone in faintly ammoniacal solution. By the use of complex-forming reagents the reaction of certain metals can be made more or less specific. Thus in ammoniacal cyanide solution only lead, bismuth, thallium, and stannous (but not stannic) tin react with dithizone.

Ferric iron does not form a dithizonate; but, depending upon the pH, it oxidizes dithizone to a greater or less extent, giving a yellow compound (diphenylthiocarbadiazone) soluble in organic liquids but not in alkaline aqueous solutions. Strong oxidizing agents such as chlorine, permanganate, etc. destroy dithizone, splitting the molecule.

The colorimetric determination of heavy metals with dithizone can be made in various ways. The "mixed-color" method has a number of advantages and will be described here with reference to copper. If an acid solution of copper is shaken with an excess of dithizone in carbon tetrachloride, the latter assumes a color varying from blue-green for very little copper to a violet for sufficient copper to react with nearly all of the reagent. The hue of the carbon tetrachloride phase can be compared with those of a series of standards, each with a constant amount of dithizone. The determination can be made more simply and more accurately by measuring the transmittancy of the dithizone-cupric dithizonate solution. A carbon tetrachloride solution of dithizone shows maximum absorption at about 620 mμ. Cupric dithizonate solution shows maximum absorption at about 550 mμ; at 620–640 mμ it absorbs comparatively little, whereas dithizone absorbs strongly in this range (Fig. 125). Consequently, by using a red filter or light of about 625 mμ, a large difference in transmittancy will be shown by solutions of dithizone and cupric dithizonate of equivalent concentrations. The standard curve is obtained by shaking constant volumes of dithizone solution with varying amounts of copper and determining the transmittancy of each solution. The results are plotted as in Figure 126. With monochromatic light a straight line is obtained, but a filter usually gives a slightly curved line.

---

[1] See the review articles, H. Fischer, Angew. Chem. *47*, 685 (1934); *50*, 919 (1937); H. J. Wichmann, Ind. Eng. Chem., Anal. Ed. *11*, 66 (1939).

[2] I. M. Kolthoff and E. B. Sandell, J. Am. Chem. Soc. *63*, 1906 (1941)

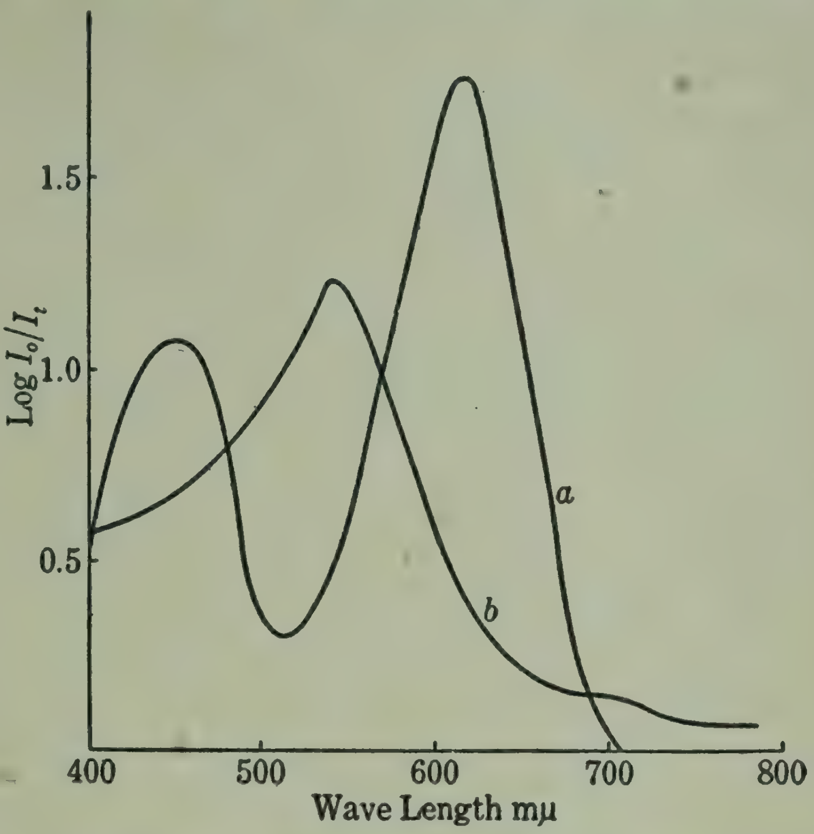


Fig. 125. Absorption curves of dithizone (a) and of keto cupric dithizonate (b) in carbon tetrachloride according to H. Fischer.

Procedure.

Special solutions:

Dithizone, 0.001–0.0012 per cent (weight/volume) in carbon tetrachloride. The latter must be reagent quality, free from any substances inhibiting the reaction with copper in acid solution. As purchased, dithizone usually contains 85–90 per cent of the active reagent. It need not be purified for this determination.

Standard copper solution, 0.100 per cent. Dissolve 0.1964 g. of clear uneffloresced crystals of $CuSO_4 \cdot 5\,H_2O$ in water, add 2 or 3 ml. of hydrochloric acid, and dilute to 500 ml. From this solution prepare a weaker one (conveniently 0.002 per cent) by dilution with 0.05 N hydrochloric acid.

Transfer the sample solution, having a volume of about 10 ml. and containing not more than 5 γ (1 γ = 0.001 mg.) of copper,[1] to a small separatory funnel. Make the solution 0.05–0.1 N in hydrochloric acid, and run in 5.0 ml. of dithizone from a covered buret. Shake for two minutes. If the color of the carbon tetrachloride is red-violet, an excess of dithizone may not be present; in such a case add another 5 ml. portion of dithizone and shake further.

Allow a few drops of carbon tetrachloride to flow out of the funnel to displace any aqueous solution in the bore of the stopcock, and dry the stem of the funnel with filter paper rolled around a thin glass rod. Deliver the carbon tetrachloride solution into a suitable cell (1 cm. thick) and cover to prevent evaporation. The solution should be entirely clear. Obtain the transmittancy of the solution at 625 mμ (a red filter may be used), using water in the reference cell.

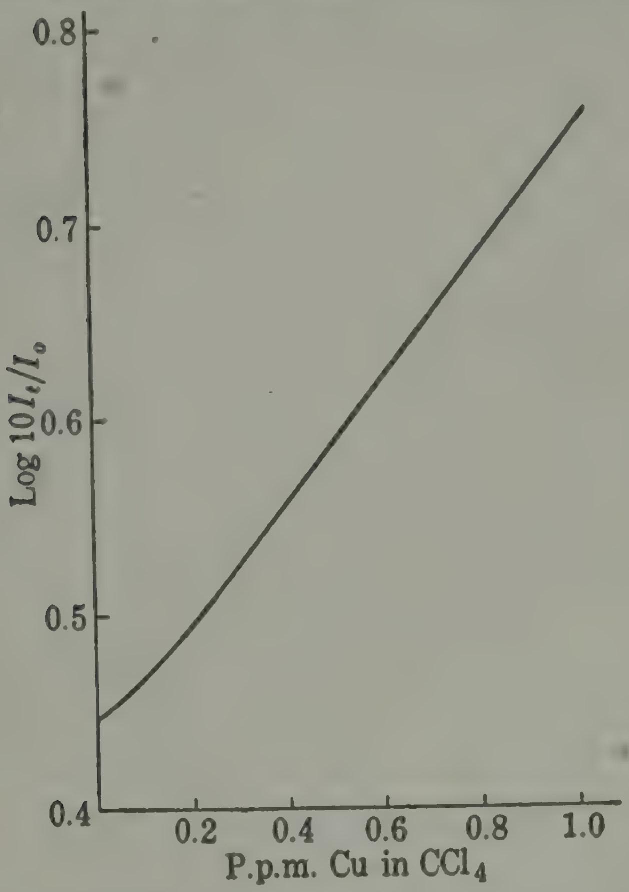


FIG. 126. Standard curve for determination of copper with dithizone (red filter.)

In constructing the reference curve, take copper solutions containing 0, 1, 2, 3, 4, and 5 γ of copper in about the same volume as the sample solution and having approximately the same acidity. Shake each solution with 5.0 ml. of dithizone. Plot log 10 I_t/I_o against copper concentration (Fig. 126).

The dilute dithizone solution is not stable and slowly becomes weaker, especially on exposure to light and in warm weather. However, once the reference curve has been established, one or two points are sufficient for checking the solution.

PROBLEMS

1. From the following data determine whether an acid solution of ferric iron with an excess of thiocyanate follows Beer's law:

% Fe	TRANSMITTANCY (1 cm.) %
0.0001	80.0
0.0002	64.5
0.0004	44.0
0.0008	22.0

2. A 1 cm. layer of a 0.0100 per cent solution of a compound having a molecular weight of 194 transmits 9.0 per cent light of wave length 490 mμ. What is the molar extinction coefficient for this wave length?

---

[1] This is the maximum amount for 5 ml. of dithizone. If the volume of the latter is increased, more copper may be taken.

3. If the molar extinction coefficient of potassium permanganate is 2235 at 520 mμ, what will be the transmittancy of a 0.0010 per cent solution in a 2 cm. cell at this wave length?

4. A solution of a colored substance has an absorption band in the range between 420 and 470 mμ with a maximum between 445 and 450 mμ. (a) What is the color of the solution? (b) What condition has to be fulfilled by other colored substances present in the solution in order not to have interference if the extinction of the unknown is determined with a spectrophotometer at a wave-length region between 447 and 450 mμ?

5. What kind of light filter would you expect to be useful in the determination of copper in ammoniacal solution?

6. The molar extinction coefficient of a colored substance with a molecular weight of 100 is equal to 10,000 in a certain solvent. Calculate the value of k in the equation:

$$\frac{I_t}{I_0} = 10^{-klc'},$$

in which c' is the concentration of the substance in grams per 100 ml.

CHAPTER XLII

METHODS IN QUANTITATIVE INORGANIC ANALYSIS

Volume determination of a precipitate.

Gravimetric, volumetric, and colorimetric analyses comprise the general methods in daily use in analytical laboratories. A great variety of other methods of more or less general applicability are available, some of which are of great use in routine analyses. In the quantitative separation of a slightly soluble compound, it is possible to determine the volume instead of the weight of the precipitate. The precipitate is formed in a centrifuge tube, the lower part of which is drawn out into a graduated capillary; and after centrifuging, all of the precipitate is collected in the capillary, and its volume is measured. This method has been recommended frequently in the literature [1] but cannot be considered accurate. The apparent volume of the precipitate depends on many factors, such as the method and conditions of precipitation, the time of standing before centrifuging, and the rate and duration of centrifuging. It is also possible that foreign constituents may affect the volume of the precipitate. Hence one can expect reproducible results only under very carefully controlled conditions. In working with barium sulfate, Greene [2] found an accuracy of only 1 to 5 per cent under the most favorable conditions.

The volumetric method of determining a precipitate by means of a pycnometer is capable of considerable accuracy, as shown by Russel.[3] The method was applied as early as 1877 by Popper,[4] who transferred such precipitates as aluminum hydroxide, barium sulfate, ferric hydroxide, mercuric sulfide, nickel hydroxide, and lead sulfate to a pycnometer along with the supernatant liquid. A similar method was used by Oknin [5] and Chatèlet,[6] but it was left to Russel to improve the technique and to show the accuracy and the advantages of the method. The pycnometric method eliminates the necessity of isolating the precipitate and transferring it to the filtering medium; even washing can frequently be omitted. Any drying, heating, or ignition of the precipitate is entirely eliminated. The pycnometric method makes possible in principle the use of precipitates which, although otherwise suitable, fail because they cannot be isolated without change in composition.

---

[1] H. Wedding, Stahl und Eisen *7*, 118 (1887); M. Ukema, *ibid.* *7*, 407 (1887); K. Bormann, Z. angew. Chem. *2*, 638 (1889); C. Reinhart, Chem. Ztg. *15*, 410 (1891); H. G. Parker, J. Am. Chem. Soc. *31*, 549 (1909); H. Friedenthal, Ber. *44*, 904 (1911); O. Arrhenius, J. Am. Chem. Soc. *44*, 132 (1922); H. J. Hamburger, Chem. Weekbl. *13*, 871 (1916); Rec. trav. chim. *35*, 225 (1915); E. R. Caley, C. T. Brown, and H. P. Price, Ind. Eng. Chem., Anal. Ed. *6*, 202 (1934).

[2] H. S. Greene, J. Am. Chem. Soc. *53*, 3275 (1931).

[3] W. W. Russel, Ind. Eng. Chem., Anal. Ed. *9*, 592 (1937); Russel and J. H. A. Harley, Jr., *ibid.* *11*, 140 (1939).

[4] R. Popper, Z. anal. Chem. *16*, 157 (1877); *18*, 14 (1879).

[5] I. V. Oknin, Zavodskaya Lab. *4*, 420 (1935).

[6] L. Chatelet, Chimie & Industrie, Special No. 199 (April, 1934).

Areametric determination of a precipitate.

Dammerell and Axelrod [1] developed a technique whereby compact circular (or square) piles of precipitate of reproducible dimensions could be obtained in the center of the bottom of a flask. The apparent areas of these spots can be measured and compared to the areas given by known amounts of precipitate. The term *areametric analysis* has been proposed for this method. Naturally, the method cannot boast of giving accurate results, but it may be useful in cases when a rapid, although highly approximate, result is desired within a short time.

Gas analysis and gasometric methods.

In this text, the analysis of only solids and liquids is considered. If the material to be analyzed is a gas, entirely different methods are used as a rule.

Generally a certain volume of the gas to be analyzed is transferred to a gas buret and the volume measured at known temperature and pressure. This volume of gas is then transferred to an absorption pipet, in which the constituent to be determined is dissolved out of the mixture with a suitable solvent or is transformed into a nonvolatile compound (e.g., CO_2 absorbed in alkali). The residual gas is then transferred back to the gas buret and the volume measured. In the calculations, the measured volumes are reduced to standard conditions of temperature (0° C.) and pressure (760 mm. of mercury). When there is no suitable absorbent for the gas to be determined, it is sometimes possible to mix it with an excess of another gas with which it reacts in a chemical way, in the presence of a suitable catalyst, and under proper conditions determine the change in volume after the reaction has taken place. Suppose, for example, that methane is to be determined in a gaseous mixture. A measured volume of the gas is mixed with a known volume of oxygen, and the methane is then burned to carbon dioxide and water. From the equation

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$$

it is evident that one volume of methane reacts with two volumes of oxygen with the formation of one volume of carbon dioxide. From the reduction in volume it is possible to calculate the methane content of the original mixture.

In the analysis of a solid or a liquid it is sometimes possible to make use of gasometric methods if the constituent to be determined can be easily transformed into a gaseous substance or reacts in a quantitative way to form a gas.

EXAMPLES:

$$CaCO_3 + 2\,HCl \rightarrow CO_2 + CaCl_2 + H_2O$$

$$2\,HNO_3 + 3\,H_2SO_4 + 6\,FeSO_4 \rightarrow 2\,NO + 3\,Fe_2(SO_4)_3 + 4\,H_2O$$

$$5\,H_2O_2 + 2\,MnO_4^- + 6\,H^+ \rightarrow 5\,O_2 + 2\,Mn^{++} + 8\,H_2O$$

$$2\,KNO_2 + 2\,KI + 2\,H_2SO_4 \rightarrow 2\,NO + I_2 + 2\,K_2SO_4 + 2\,H_2O.$$

---

[1] V. R. Dammerell and M. Axelrod, J. Am. Chem. Soc. *57*, 2724 (1935).

REFERENCES

The following books on gas analysis may be mentioned:

L. M. Dennis and M. L. Nichols, *Gas Analysis*, revised ed., The Macmillan Co., New York, 1929.

W. Hempel, *Methods of Gas Analysis*, translated by L. M. Dennis, The Macmillan Co., New York, 1892.

A. H. White, *Gas and Fuel Analysis*, 2d ed., McGraw-Hill Book Co., New York, 1922.

L. W. Winkler-Brunck, *Lehrbuch der technischen Gasanalyse*, 5th ed., Felix, 1927.

A. H. Gill, *The Analysis and Handling of Gases*, Edward Brothers, Inc., Ann Arbor, 1934.

H. A. Daynes, *Gas Analysis by Measurement of Thermal Conductivity*, Cambridge University Press, London, 1933.

Catalytic methods.

Various slow reactions may be accelerated by the addition of a catalyst. In many cases the catalytic effect of a substance is specific and proportional to the concentration of the catalyst within certain limits. Therefore by a quantitative measurement of the catalytic effect, it is often possible to determine a particular substance, even in extremely small concentrations.

Many reactions (e.g., inversion of sucrose, decomposition of diazoacetic ester) are catalyzed by hydrogen ions, and it has been found that the reaction velocity, within certain limits, is proportional to the hydrogen-ion concentration. Other acids besides the H_3O^+ ion exert a similar effect but to a lesser degree.[1]

The reaction between ceric sulfate and arsenious acid in acid medium occurs very slowly but is strongly catalyzed by traces of iodide or osmium. Use is made of this catalysis in the determination of minute traces of iodide or osmium.[2]

Catalytic methods are especially useful in the determination of substances present in such low concentrations that other methods fail to give any results. However, great care should be observed in interpreting results obtained by catalytic methods, because various other factors may influence the reaction velocity.[3]

Physico-chemical methods of analysis.[4]

Substances are distinguished by their *properties*. Any property which can be measured in a *quantitative way* can be made use of in quantitative analysis.

---

[1] For a review of acid-base catalysis, see J. N. Brönsted, Chem. Rev. *5*, 232 (1928).

[2] E. B. Sandell and I. M. Kolthoff, J. Am. Chem. Soc. *56*, 1426 (1934).

[3] See I. M. Kolthoff and R. S. Livingston, Ind. Eng. Chem., Anal. Ed. *7*, 209 (1935).

[4] For application of various physico-chemical methods in analytical chemistry, see: W. Böttger, *Physikalische Methoden der analytischen Chemie*, Akad. Verlagsges., Leipzig, Vol. I, 1935; Vol. II, 1937; Vol. III, 1939; Peter Wulff, *Anwendung physikalischer Analysenverfahren in der Chemie*, Verlag Müller und Steinicke, München, 1936.

An excellent review of "Instrumental Methods of Chemical Analysis" with photographs of apparatus, application to industrial analysis, and a complete bibliography is given by R. H. Müller, Ind. Eng. Chem., Anal. Ed. *13*, 667 (1941).

There are certain properties which all substances have in common but whose *numerical values* are different, such as density or refractive index. These are *unspecific properties*, and their application to quantitative analysis is rather limited, since each component present in the mixture will affect the numerical value of the property measured.

There are relatively few properties which are specific for a particular substance or element. The emission spectrum and the absorption spectrum for visible and invisible light are specific properties, and their quantitative application to chemical analysis is therefore very general.

Between these two extremes there are properties which are intermediate between the unspecific and specific ones. For example, only electrolytes contribute to the electrical conductivity of aqueous solutions, or only those organic substances containing an asymmetric carbon atom rotate the plane of polarized light.

From the above it is evident that the quantitative use of unspecific properties is mainly limited to simple binary mixtures. By the determination of the density or the refractive index of a solution of one component in a solvent, it is possible to find the amount of solute accurately. If a third substance is also present in the solution, the determination of the specific gravity alone does not enable us to find the individual amounts of both solutes. In such a case it may be possible to find the amounts of both constituents by measuring a second unspecific property such as the refractive index.

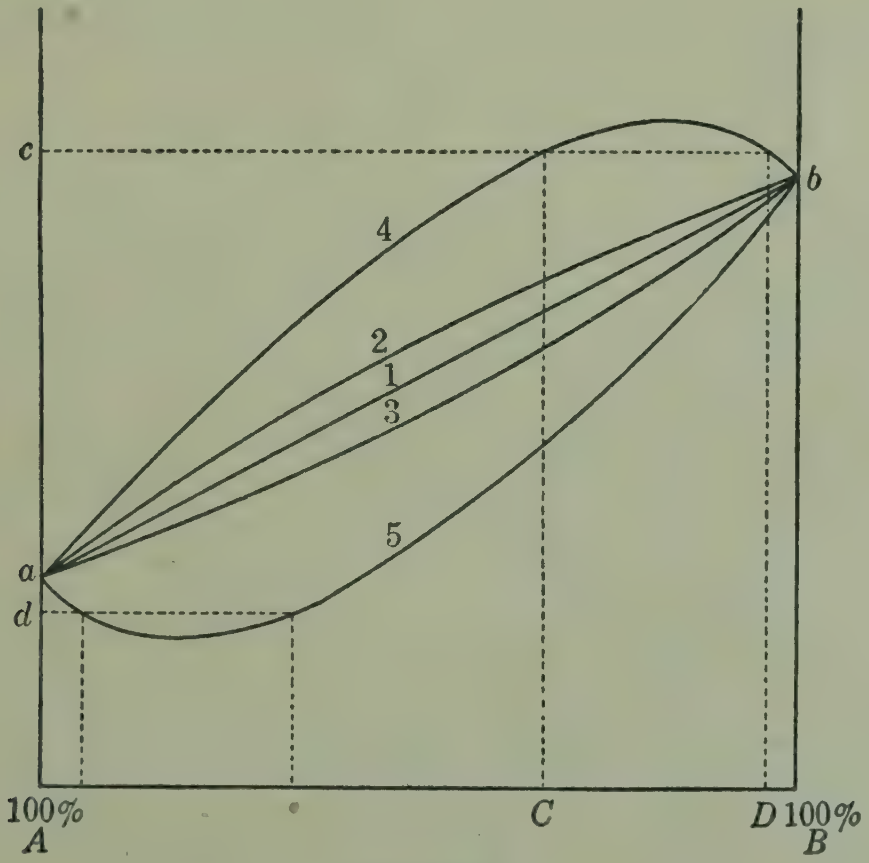


FIG. 127

It is not always possible to derive the concentration of the solute in a binary mixture from the measurement of one unspecific property. In Figure 127 point *a* gives the numerical value of the unspecific property of the pure substance *A*, and point *b* that of pure substance *B*. On going from 100 per cent *A* to 100 per cent *B*, the numerical value of the property as a rule does not change linearly or, in other words, not according to the straight line 1. If the latter would give the numerical value of a property of a mixture of A and B, the composition of any mixture could be easily calculated from the numerical value of a property of the mixture and the values of the same property of pure A and B. Suppose, for example, that the mixture contains x per cent B; then it contains $(100 - x)$ per cent A. The following relation holds:

$$100 \cdot m = (100 - x)a + x\,b$$

where m denotes the numerical value of the property of the mixture. As a rule, however, there is no linear relation as represented by line 1; curves of types such as 2 or 3 in Figure 127 represent the more general case. Even then it is possible to derive the composition of a binary mixture from a single measurement of an unspecific property, either graphically or with the aid of suitable tables.

The matter becomes more involved if the curve giving the numerical values of the properties of mixtures of A and B shows a definite maximum (curve 4) or minimum (curve 5). If we are dealing with the case represented in curve 4, it is easily seen that any measured value greater than b corresponds to two different compositions of the mixture. Let the value measured be equal to c. The composition may then correspond either to C (ratio $A : B = BC : AC$) or to D (ratio $A : B = BD : AD$). Usually there are simple methods for deciding which of the two is being dealt with.

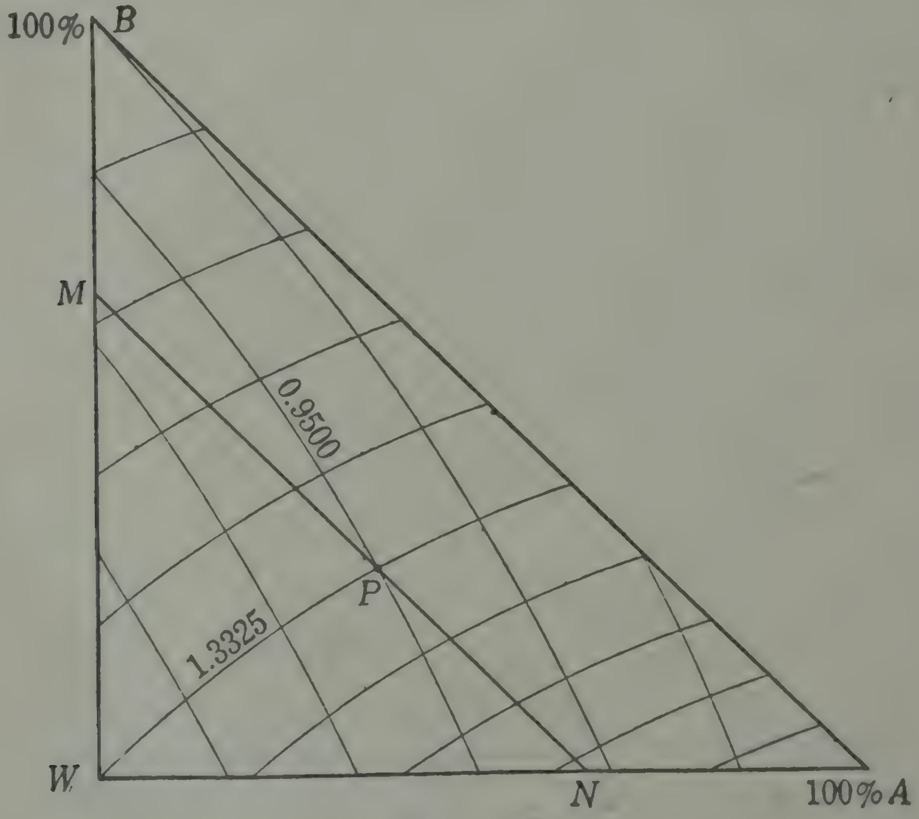


FIG. 128

If we are dealing with a ternary mixture, the measurement of one property does not suffice to find the composition. Determination of the values of two different unspecific properties often enables us to solve the problem in a graphical way, as illustrated in Figure 128.

BWA is a right-angled triangle in which $BW = WA$. Let W represent pure water, B the pure solute B, and A the pure solute A. Points on the line WB indicate mixtures of water and B, whereas points on WA correspond to mixtures of water and A. Any point in the triangle represents a mixture of W, A, and B, the composition of which may be found graphically. If P be such a point, it is seen that the corresponding mixture contains $MB = NA$ per cent water and $(100 - MB) = (100 - NA)$ per cent of B plus A, the latter in a ratio of PN of B to PM of A. Empirically the numerical values of two unspecific physical properties, say the density and the refractive index, are determined for a great number of mixtures of varying composition. The lines in the figure represent respectively the compositions of mixtures having the same density and the compositions of mixtures having the same refractive index. The density and the refractive index of the unknown are now determined. Suppose that the former value is 0.9500 at 25°; then the composition of the unknown must lie on some point of the line marked 0.9500. If the refractive index is 1.3325, the composition must be on the line marked 1.3325. Evidently the point of intersection, P, of these two lines gives the composition of the unknown. Actually, as a rule, one will plot not the entire diagram BWA but only a small part of it on a large scale in order to make more accurate interpolation, if necessary.

Theoretically it would be possible to make a similar physico-chemical analysis if three solutes were present in the solution. In this case three properties would have to be measured. However, the solution becomes less simple, and moreover small errors in the determination of the physical properties may affect the results very seriously.

In the following, some physico-chemical methods are mentioned.

REFERENCES

For numerical values of properties of substances and mixtures, the student is referred to extensive tables to be found in the following:

International Critical Tables of Numerical Data, 7 vols. and index, published by the National Research Council, McGraw-Hill Book Co., New York, 1926–1933.

Landolt-Börnstein-Roth, *Physikalisch chemische Tabellen*, edited by W. A. Roth and K. Scheel, and supplementary volumes, J. Springer, Berlin, 1923.

Tables annuelles de constantes et donnees numeriques, Gauthiers-Villars et Cie, Paris; McGraw-Hill Book Co., New York.

Handbook of Chemistry and Physics, Chemical Rubber Publishing Co., Cleveland (Ohio), 1943.

Lange's *Handbook of Chemistry*, Handbook Publishers, Inc., Sandusky (Ohio), 1941.

The performance of physico-chemical determinations is described in texts and handbooks on this field:

J. Reilly and W. N. Rae, *Physico-chemical Methods*, 3d ed., 2 vols., Methuen and Co., London, 1940.

Ostwald-Luther, *Physiko-chemische Messungen*, edited by C. Drucker, 4th ed., Akademische Verlagsgesellschaft, Leipzig, 1925.

A. Stähler, *Handbuch der Arbeitsmethoden in der anorganischen Chemie*, 4 vols., Veit & Co., Leipzig, 1913–1926.

W. N. Lacey, *Instrumental Methods of Chemical Analysis*, The Macmillan Co., New York, 1924.

Density.

Density measurements are widely used for the determination of the composition of binary mixtures. The density is determined with a pycnometer, or by the hydrostatic method (balance of Mohr-Westphal, hydrometers). The determination of alcohol is an example of an important analysis made by density measurements.[1]

Refractive index.

The refractive index, like density, is an unspecific property. Usually it is determined with the Abbé (universal) refractometer or with the immersion refractometer. For the determination of the refractive index of very dilute solutions or for the accurate determination of the difference in refractive index of two solutions of nearly the same composition, the interferometer is applied. The latter also finds important use in gas analysis.[2]

Electrical conductivity.

Water is a poor conductor of electricity, the specific conductance of the purest water being of the order of 0.4×10^{-7} reciprocal ohms at 25°. Solutions of both weak and strong electrolytes increase the conductance, but in the case of the latter the conductance does not increase linearly with the concentration. The conductivity method is very suitable for the determination of the concentration of a dilute as well as a more concentrated solution of an electrolyte. The conductivity increases greatly with increasing temperature (*ca.* 2 per cent per degree), and in accurate measurements the latter should be controlled to within 0.01° C.

An application of the conductance method is sometimes made in the determination of traces of water in organic solvents, especially in the alcohols. The conductivity of an acid in ethanol decreases very strongly upon addition of small amounts of water. If the conductance of an acid of a certain concentration in alcohol containing varying amounts of water has been determined, the water content of the unknown is found by measuring the conductance of a solution of the acid of the same concentration, in the unknown sample.[3]

---

[1] J. Domke and E. Reimerdes, *Handbuch der Aräometrie*, J. Springer, Berlin, 1912.

[2] For a discussion and literature references, see Fritz Löwe, *Optische Messungen des Chemikers und des Mediziners*, 2d ed., Verlag Theodor Steinkopff, Dresden, 1933; W. A. Roth and F. Eisenlohr, *Refraktometrisches Hilfsbuch*, Veit & Co., Leipzig, 1911.

[3] F. Kohlrausch and L. Holborn, *Das Leitvermögen der Elektrolyte*, B. G. Teubner, Berlin, 1916; H. T. S. Britton, *Conductimetric Analysis; Principles, Technique, Application*, Chapman and Hall, London, 1934; K. Sandera in *Physikalische Methoden der Analytischen Chemie*, 1935, 1937, 1939.

For the conductometric determination of water in alcohol see H. Goldschmidt and F. Aas, Z. physik. Chem. *112*, 423 (1924), where further literature references may be found. For conductometric titrations, see p. 509.

Polarography (Voltammetry).

The principle of the polarographic method of analysis is described in the section "Amperometric Titrations." The electrolysis method with the dropping-mercury electrode finds wide application in inorganic and organic analysis. The electrolyzed substances are characterized by their "half-wave potentials," and their concentrations are found from the magnitude of the "diffusion current." When dealing with a mixture of electroreducible substances, the concentration of each is found from the corresponding diffusion current. The theory and the practical application of polarography and voltammetry are covered in a recent monograph.[1]

Dielectric constant.

Measurements of the dielectric constant may be of analytical importance in a study of a mixture of two liquids which are nonelectrolytes. Various interesting examples are mentioned by L. Ebert,[2] who also applies the method to the determination of water in strongly hygroscopic solids.

Thermometric methods.

In certain cases the amount of a constituent can be determined by measuring the change in temperature upon addition of a suitable reagent. In inorganic analysis such methods are rarely used (cf. chapter on Physico-chemical Determination of the End Point, p. 502).

Chronometric methods.

Methods have been proposed in which the time required for the appearance of a precipitate or a color after the addition of a suitable reagent is noted and the concentration of the unknown found therefrom. This method, for example, has been suggested for the determination of small amounts of sulfate in water. The time after which a precipitate becomes visible upon addition of a barium solution decreases with increasing sulfate concentration. Such methods are not very accurate. In addition, the time required for the first visible formation of a precipitate depends on various factors. The presence of foreign constituents, especially, may have an appreciable effect upon the results.

Polarimetry.

Organic substances containing an asymmetric carbon atom rotate the plane of polarized light and are said to be *optically active*. Asymmetric tetravalent compounds of tin, sulfur, selenium, silicon, and those of pentavalent nitrogen are also optically active. The angle of rotation of the plane of polarized light produced by a solution of an optically active substance is determined in a *polarimeter*. The following relation exists:

$$[\alpha]_D^{20} = \frac{a}{lc}$$

in which a is the observed angle of rotation in degrees, l the length of the tube in decimeters, c the concentration expressed in grams per ml. of solution; $[\alpha]_D^t$ represents the specific rotation for sodium (D) light at a temperature t, and is equal to a when l and c are equal to 1. Actually the specific rotation is not an absolute constant but depends (in addition to the temperature and the kind of light used) upon the concentration and presence of other substances. The polarimetric method is chiefly used in organic analysis, especially in the analysis of sugars, essential oils, and alkaloids.[1] Polarimetry finds rare application in inorganic analysis. However, various inorganic compounds can be determined polarimetrically by virtue of the fact that they form complexes with optically active molecules in which the rotation of the latter is altered markedly (e.g., molybdate with tartaric acid and tartrates).

---

[1] I. M. Kolthoff and J. J. Lingane, *Polarography*, Interscience Publishers, Inc., New York, 1941.

[2] L. Ebert, Z. angew. Chem. *47*, 305 (1934). See also P. Cohen Henriquez Rec. trav. chim. *54*, 327 (1935).

Whereas optical rotation is shown by relatively few substances, it is found that the *magnetic rotation* of plane-polarized light is exhibited by all transparent substances whether solid, liquid, or gaseous. The measurement of magnetic rotation, although an important tool in research, has not found direct analytical application.

Surface tension.

Dissolved substances change the surface tension of the solvent. Most inorganic substances increase the surface tension of water, but the effect is relatively small and of no analytical importance. Various organic substances decrease the surface tension of water materially, especially in relatively dilute solutions; such substances are said to be capillary active. The concentration of such a substance may be found by determining the surface tension of the solution.[2]

Viscosity and fluidity.

When a body is moved through a liquid, it meets with a resistance which tends to stop the motion. This resistance is due to the "viscosity" of the liquid. A liquid, such as ether, which is very mobile, has a relatively small viscosity, whereas glycerol or a concentrated sugar solution, which is syrupy in character, shows a relatively high viscosity. Although the viscosity of water is changed by a solute, hardly any use is made of viscosity determinations in quantitative inorganic analysis. Such determinations are of more importance in organic analysis, especially in the evaluation of mineral oils. Measurements of viscosity are as a rule made by the determination of the rate of flow of a liquid through a capillary tube under definite conditions. The apparatus is called a viscometer.[3]

---

[1] H. Landolt, *Optical Rotation of Organic Substances*, 2d ed., The Chemical Publishing Co., Easton, Pa., 1902. G. W. Rolfe, *The Polariscope in the Chemical Laboratory*, The Macmillan Co., New York, 1905. *Polarimetry, Saccharimetry, and the Sugars*, Circular of the Bureau of Standards, No. 440, 1942. C. A. Browne and F. W. Zerban, *Physical and Chemical Methods of Sugar Analysis*, John Wiley and Sons, New York, 1941.

[2] H. Freundlich, *Kapillarchemie*, 3d ed., Akademische Verlagsgesellschaft, Leipzig, 1932. R. S. Willows and E. Hatschek, *Surface Tension and Surface Energy*, P. Blakiston's Son & Co., Philadelphia, 1923. E. K. Rideal, *Surface Chemistry*, University Press, Cambridge, 1930.

[3] A. E. Dunstan and F. B. Thole, *The Viscosity of Liquids*, Longmans, Green & Co., London, 1914. E. G. Bingham, *Fluidity and Plasticity*, McGraw-Hill Book Co., New York, 1922. E. Hatschek, *The Viscosity of Liquids*, G. Bell & Sons, Ltd. London, 1928.

Miscibility.

When two liquids are only partially soluble in each other, they may separate into two layers after mixing. Increase of temperature as a rule increases the mutual solubilities, and often a temperature is found above which the two liquids are completely miscible in any ratio. This temperature is called the *critical solution temperature.*

Two liquids which are miscible in any ratio at room temperature may separate into two phases on addition of a third substance. Alcohol and ligroin, for example, are completely miscible. However, on addition of water the solution becomes turbid, and two layers are formed. Upon heating in a closed tube, the two layers again become miscible at a certain temperature. This temperature is best determined from the "high" side, by heating to a temperature where only one phase exists. On careful cooling with stirring the appearance of a turbidity denotes the re-formation of two phases, and the temperature at which this phenomenon occurs can be read. The determination of the critical solution temperature is an important tool in the investigation of the water content of various organic solvents (for example of alcohols; Crismer Number)[1] and can yield highly accurate results.

Freezing-point lowering, boiling-point elevation, osmotic pressure, vapor tension.

These properties are of little use in analytical work, although in special cases applications may be made (testing of milk for water by the cryoscopic method.)

Radioactive determinations.

When dealing with radioactive elements the amounts present in the sample are as a rule so small that they cannot be determined chemically. Even if a purely chemical determination were possible, it often would not be applicable owing to the presence of inactive isotopes. In the determination of radioactive elements the α, β, or γ radiation — depending upon the case — is measured with an electroscope. Gamma-ray electroscopes have served for the determination of as little as 10^{-10} g. of radium. Smaller quantities, for example in rocks, may be measured more accurately by the emanation method. The same method is used for the indirect determination of uranium in rocks, it being assumed that there is a constant uranium-radium ratio. Alpha-ray electroscopes are used for measuring thorium B and C deposits, and polonium. Beta-ray measuring devices are required for preparations containing uranium X, radium D and E, and may be used for thorium B and C.[2]

Colorimetry, spectrophotometry.

Determinations based upon the measurement of the amount of light absorbed by a solution have been discussed in the chapter on Colorimetry. If monochromatic light is used — either visible, ultraviolet, or infrared light — the method becomes highly specific (spectrophotometric analysis) References are given in Chapter XLI (p. 645).

---

[1] L. Crismer, Bull. Soc. Chim. Belg. *18*, 4 (1904); L. de Brouckère and A. Gillet, *ibid.* *44*, 473 (1936).

[2] S. C. Lind, Ind. Eng. Chem. 7, 1024 (1915). H. H. Barker and H. Schlundt, Univ. of Missouri Bulletin *24*, No. 26; Eng. Expt. Series, *23* (1923). F. Paneth and W. Bothe, *Handbuch der Arbeitsmethoden in der anorganischen Chemie*, Vol. II, p. 1027, de Gruyter, Berlin (1925)

Turbidimetry, nephelometry.

Wells,[1] who has written an excellent paper on the "Present Status of Turbidity Measurements," makes the following statement: "Every attack on the problem of disperse systems is disappointing, because of the baffling complexity of the phenomena. Diaphanometers, nephelometers, turbidimeters, tyndallmeters, dispersimeters, opacimeters, have been developed and placed on the market but not one has yet been accepted as a standard instrument for the laboratory. . . . Apparently turbidity measurements have not proven satisfactory and yet the prospects are more hopeful than they seem. Once the limitations of such optical methods are understood, their real possibilities will be appreciated for what they are worth."

Light which has traversed a *turbid* medium is less intense than the incident light. This decrease in intensity is caused by:

(a) *Extinction* (selective absorption). The light waves penetrate the particles in the suspension and are transformed into heat. The suspension will show a color if the different wave lengths of the visible spectrum are absorbed to different degrees.

(b) *Radiation.* The particles *reflect* and *refract* the light in all directions.[2]

The concentration of a suspension can be measured in two ways:

1. By measuring the amount of light transmitted, which can be done in a suitable colorimeter or a spectrophotometer. In this way the diffuse density of the suspension is determined, and the instrument used is a *turbidimeter.* Owing to secondary effects, Beer's law, which holds for molecular absorption (dilution law: $l \times c$ = constant; see p. 648), holds in suspension only for very thin layers or very dilute suspensions.

2. By measuring the intensity of the scattered light (Tyndall light), i.e., the ratio of the Tyndall intensity to that of the incident light. Instruments which measure the Tyndall ratio directly are called *tyndallmeters;* but when the sample is compared with a standard of known concentration (dispersity), they are called *nephelometers.* These are used in analytical work, especially for the measurement of the concentration of very dilute suspensions; for more concentrated suspensions turbidimeters should be employed.

Principle of the nephelometer. Uniform and constant light falls at right angles upon two tubes containing the suspensions. The tubes are similar to the cups of a colorimeter (see p. 657) but have black glass bottoms fused to transparent sides. The depth of the layer in the cup in which the scattering takes place is adjustable by black glass plungers with fused-in, optically-plane bottoms. The rest of the instrument is comparable to the colorimeter.[3] Both cups are filled with a standard suspension of the substance to be determined; and one side, say the standard, is set at exactly 20.0 or 30.0. One now adjusts the plunger in the other cup until equal light intensity in the two cups is obtained. A series of five to ten settings gives an average. The standard is discarded and the cups filled, say with a standard containing half the concentration of the original one. The setting in the other cup is left unchanged. If Beer's law holds, the reading of the one-half standard should read exactly twice that of the standard. By changing the concentration of one of the standards, a calibration curve is obtained. The latter will be a curve and not a straight line, since Beer's law does not hold over a wide range of concentrations or depths of the layer. For practical purposes it may be assumed that Beer's law holds, if the concentration of the suspension in one cup is within 25 per cent of that in the other cup. Therefore if the concentration of the unknown suspension is roughly known, a known suspension of approximately the same concentration prepared under identical conditions can be used as a standard in one of the cups. Again both cups are filled with the same standard suspension, one plunger being set at a fixed mark and the other adjusted to equal light intensity. If the instrument were perfect, the readings would be the same; but this is rarely the case. In the above procedure the imperfections of the instrument are eliminated. Work with a nephelometer requires much experience. Under the most favorable conditions a relative accuracy of 2 per cent can be attained. Especially in working with precipitates of small molecular weight, it is extremely hard to obtain this accuracy, because the reproducibility of the suspension is usually extremely poor. *The reproducibility of a suspension is one of the most important conditions to be fulfilled in accurate nephelometric work.*

---

[1] P. V. Wells, Chem. Rev. *3*, 331 (1927).

[2] For a theoretical discussion of the behavior of scattering media, see H. J. Channon, F. F. Renwick, and B. V. Storr, Photogr. J. *58*, 121 (1918).

[3] For an elaborate discussion of different types of nephelometers, see J. H. Yoe, *Photometric Chemical Analysis,* Vol. II, *Nephelometry,* John Wiley and Sons, New York, 1929.

The theory of the scattering of light by very small particles was given by Lord Rayleigh.[1] The intensity I_s of light scattered from N particles each of volume v, the intensity of the incident light being I_0 and the wave length λ is:

$$I_s = I_0\left[\frac{(n'^2 - n^2)Nv^2}{n^2\lambda^4r^2}(1 + \cos^2\beta)\right]$$

Here n represents the refractive index of the medium, and n' that of the particles. The particles are supposed to be contained in such a small volume that the distance r and the angle β between the scattered and incident rays are the same for all particles. When the particles are not small compared with the wave length, terms of higher order must be included, and the equation becomes very complicated. No account is taken in the equation of secondary scattering. When the medium is densely filled with particles, this factor may become of prime importance, causing deviation from Beer's law.

The most striking characteristic of the equation is the occurrence of the factor $\frac{1}{\lambda^4}$, indicating that the amount of scattered light increases rapidly as the wave length decreases. Using white light as a light source, the scattered light is therefore much bluer than the incident light, while the blue is correspondingly absent in the transmitted portion, which contains a relatively large fraction of the red light (turbidimetry). The equation of Rayleigh gives a far from complete picture of the intensity of scattered light, as various studies published on this subject in the literature show. Rayleigh assumed the particles to be dielectrics. A theory of scattering by small particles, assuming them to be perfect conductors (particles in a metal sol), was worked out by Thomson.[1] Maxwell-Garnett[2] and Mie[3] have extended the theory to larger particles and imperfect conductors.[4]

---

[1] J. W. Strutt (Lord Rayleigh), Phil. Mag. *41*, 107 (1871).

From the analytical viewpoint it is important to realize that the amount of scattered light increases, according to Rayleigh's equation, with increasing size of the particles, the total amount of suspended material remaining the same. With barium sulfate suspensions in glycerol, Bechhold and Hebler[5] found a maximum Tyndall effect at a size of 0.84 μ; Owe[6] found the maximum at *ca.* 0.2 μ with the same dispersions.

If two suspensions of the same substance containing the same amount of dispersed material are compared in the nephelometer, the readings will be the same only when the particles have the same sizes. If this condition is not fulfilled, the suspension with the largest particles will show the greatest amount of scattered light. Successful nephelometry (also turbidimetry) therefore depends not only on a satisfactory instrument but equally as much on a satisfactory method of producing the precipitate to be measured.[7] This must be such that a given weight of the substance to be measured will always produce a precipitate of the same optical quality. Hibbard, for example, mentions that by varying the concentration and the manner of mixing the reagents it is possible to produce a precipitate of barium sulfate having two to three times more opacity than another produced from the same amount of sulfate.

The following factors are of great importance in nephelometric determinations:

1. The concentration of the two ions which combine to produce the precipitate.
2. The ratio of concentrations in the solutions mixed.
3. The manner of mixing.
4. The rate of mixing.
5. The time required to produce maximum scattering (or turbidity).
6. The stability of dispersion.
7. The temperature.
8. The presence of other electrolytes.

---

[1] J. J. Thomson, *Recent Researches in Electricity and Magnetism*, p. 437, Oxford, 1893.

[2] J. C. Maxwell-Garnett, Phil. Trans. *203*, 385 (1904); *205*, 237 (1906).

[3] G. Mie, Ann. Physik. *25*, 377 (1908); literature review, see F. B. Gribnau, Thesis, Utrecht, 1935.

[4] Compare also N. Pihlblad, Z. physik. Chem. *92*, 471 (1917); T. Teorell, Kolloid Z. *53*, 322 (1930); *54*, 58, 150 (1931).

[5] H. Bechhold and F. Hebler, Kolloid Z. *31*, 70 (1922).

[6] A. W. Owe, Kolloid Z. *32*, 73 (1923).

[7] P. L. Hibbard, J. Ind. Eng. Chem. *16*, 804 (1924).

9. The presence of nonelectrolytes. The solubility of most inorganic precipitates is decreased by the addition of organic solvents immiscible with water. Since the degree of supersaturation then increases, the number of particles formed increases also, and the amount of light scattered or absorbed decreases in the presence of organic solvents. However, the effect of the variation of the refractive index with the change of the medium also should be considered. The organic solvents stabilize the suspensions.

10. If the suspensions settle too rapidly, more stable ones are frequently obtained by precipitation in the presence of a protective colloid. Again the particle size will be found to be entirely different when the suspension is prepared in the absence than in the presence of protective colloids.

Finally, it may be mentioned that in turbidity measurements instruments are sometimes used in which the depth at which a target disappears beneath the layer of a turbid medium is determined. This method is very simple but not very accurate.

IMPORTANT REFERENCES

Theory:

P. V. Wells, Chem. Reviews *3*, 331 (1927).

Practical performance and instruments:

J. H. Yoe, *Photometric Chemical Analysis*, Vol. II, *Nephelometry*, John Wiley and Sons, New York, 1929.

F. V. von Hahn, *Dispersoidanalyse*, Theodor Steinkopff, Dresden, 1928.

Quantitative spectroscopy.

Spectrography. In spectroscopy use is made of the emission spectra of elements produced in a flame, arc, or spark. By analyzing the emitted light in a spectroscope, a line spectrum is obtained, consisting of a series of lines at wave lengths characteristic of each element.

The spectroscopic method has been in use for a long time in the sensitive detection of many elements (Bunsen, Kirchhoff). Spectrum analysis for quantitative purposes was introduced by Lockyer[1] and Hartley[2] and has been developed to a great extent since. The intensities of various lines of an element are different, and in general the intensity of a given line is proportional to the concentration of the element. On dilution, the weakest lines will disappear first, and finally a concentration is reached at which only the most persistent lines (*raies ultimes* of de Gramont)[3] remain. By photographing the spectra at various dilutions of sample and observing the lines which are left, it is possible to estimate in an approximate way the concentration of the element. A refinement which largely eliminates differences caused by variations in photographic conditions consists in photographing the spectrum of the sample on the same plate with that of a series of standard samples.

More accurate is the method in which the intensity of a certain line is determined by a photometric method and compared with a nearby line of another element present at a constant concentration. This "internal standard method" was developed by Gerlach [1] and Schweitzer.[2] Scheibe and Neuhäusser [3] and Twyman and Hitchen [4] made use of a rotating logarithmic sector placed before the spectrograph, by which the length of the line in the spectrum becomes proportional to the concentration of the element.

---

[1] N. Lockyer, Phil. Trans. *164*, 749 (1874).

[2] W. N. Hartley, Phil. Trans. *175*, II, 49, 325 (1884).

[3] A. de Gramont, Ann. chim. phys. [8], *17*, 437 (1909); Ann. chim. *3*, 269 (1915).

In general the application of quantitative spectroscopy requires much experience; routine methods have been given for the determination of traces of impurities in alloys. The main advantages of the spectroscopic method are the following: The method is specific for the element to be determined, although difficulties arise when a line of another element present overlaps that of the unknown. The method is time-saving; it allows the quantitative determination of traces of elements in a sample, especially in an alloy — without any preliminary treatment. In addition a permanent record is obtained on the photographic plate. By spectrographic analysis the following impurities in tin could be determined directly: Cu, 0.1; Pb, 0.1; Fe, 0.005; Zn, 0.001; Ni, 0.001 per cent.[5]

A distinct disadvantage of the spectrographic method is that its accuracy is far below that of gravimetric, volumetric, or colorimetric procedures. With instruments of the highest refinement an accuracy of 5 per cent may be obtained, but as a rule it is less than 10 per cent. Of course, it should be realized that the spectrographic method is mainly applied to the determination of traces of impurities in alloys and other materials where conventional methods become difficult, fail, or give less accurate results. Moreover, the intensities of the lines in the spectrum are sometimes affected by the presence of other elements. With the use of a flame spectrum the intensity of the spectral lines may depend upon the kind of anion present, since the latter may determine the degree of volatility. There is a voluminous literature on the field of spectrography.

REFERENCES

E. C. C. Baly, *Spectroscopy*, Vols. I–III (1927), Longmans, Green & Co., London.

W. Gerlach and E. Schweitzer, *The Foundations and Methods of Chemical Analysis by the Emission Spectrum*, translated from the German, Adam Hilger, Ltd., London, 1931.

W. Gerlach and W. Gerlach, *Die chemische Emissionsspektralanalyse*, Vol. I (1930), Vol. II (1933), Vol. III (1936), Leopold Voss, Leipzig.

H. Lundegärdh, *Die quantitative Spektralanalyse der Elemente*, 2d ed., G. Fischer, Jena, 1934.

D. M. Smith, *Metallurgical Analysis by the Spectrograph*, British Non-Ferrous Metals Research Association, London, 1933; Bibliography, 1935.

---

[1] W. Gerlach, Z. anorg. allgem. Chem. *142*, 383 (1925).

[2] E. Schweitzer, Z. anorg. allgem. Chem. *164*, 127 (1927).

[3] G. Scheibe and A. Neuhäusser, Z. angew. Chem. *41*, 1218 (1928).

[4] F. Twyman and C. S. Hitchen, Proc. Royal Soc. A. *133*, 72 (1931).

[5] See, for example, W. F. Meggers, C. C. Kiess, and F. J. Stimson, Bur. Standards Sci. Paper No. 444 (1922).

Various publications obtainable from Adam Hilger, Ltd., London, concerning spectrum analysis.

Instruments for Spectrographic Analysis, Bausch & Lomb Optical Co., Rochester, N. Y., 1932.

H. Kayser and H. Konen, *Handbuch der Spektroskopie* (8 vols.), S. Hirzel, Leipzig, 1932.

J. A. Radley and J. Grant, *Fluorescence Analysis in Ultraviolet Light*, D. Van Nostrand Co., Inc., New York, 1933.

P. W. Dankworth, *Lumineszenz-Analyse*, Akademische Verlagsgesellschaft, Leipzig, 1922.

Judd Lewis, *Spectroscopy in Science and Industry*, Blackie & Son, Ltd., London and Glasgow, 1933.

W. Seith and K. Ruthardt, *Chemische Spektralanalyse*, J. Springer, Berlin, 1938

On X-ray spectroscopy see:

G. v. Hevesy, *Chemical Analysis by X-rays and Its Applications*, McGraw-Hill Book Co., New York, 1932.

M. Siegbahn, *The Spectroscopy of X-Rays* (translated by G. A. Lindsay), Oxford University Press, 1925.

Physikalische Methoden der analytischen Chemie, spektroskopische und radiometrische Analyse, G. Scheibe (Spectrography, Spectrophotometry); H. Mark (X-Ray spectroscopy); R. Ehrenberg (Radiometric methods); Akademische Verlagsgesellschaft, Leipzig, 1930.

Microscopical methods.

Microscopical methods are those in which a microscope is used. Such methods can sometimes be applied when other methods fail; they are particularly valuable in the quantitative analysis of complex heterogeneous mixtures which are not readily amenable to ordinary chemical methods.[1] To determine the relative amounts of the components of a powdered mixture, the number of particles of each may, for example, be counted under the microscope. The *numerical* percentages thus obtained can be converted into weight percentages if the density of each component is known; if necessary, account is taken of the difference in particle size of the various components. To be sure, such a method does not give results of high accuracy; but not infrequently an analysis can be made in no other way, and, moreover, the time required is usually not great. In an analogous manner the percentages of the components of a compact material such as a rock, an ore, or an alloy can be found by measuring microscopically the linear or areal intercepts of the components in a prepared section of the material.[2]

The microscope also serves for the indirect measurement of very small masses beyond the sensitivity limits of the microbalance. Thus the weights of small spheres of gold, platinum, mercury, etc. obtained by suitable procedures can be found by determining their diameters with a microscope micrometer.[1] Even the analysis of a minute amount of gas in the form of a spherical bubble can be based on this principle.[2]

---

[1] See E. M. Chamot and C. W. Mason, *Handbook of Chemical Microscopy*, Vol. I, p. 431, John Wiley and Sons, New York, 1938.

[2] See the work of Chamot and Mason cited in the preceding footnote, and also A. Johannsen, *Manual of Petrographic Methods*, 2d ed., p. 291, McGraw-Hill Book Co., New York, 1918.

[1] For an application of this method see G. Lunde, Mikrochem. 5, 16, 102 (1927).

[2] A. Krogh, *Abderhaldens Handbuch der biochemischen Arbeitsmethoden*, Vol. 8, p. 495, Berlin, 1915.

ANALYSES OF COMPLEX MATERIALS

CHAPTER XLIII

ANALYSIS OF BRASS

Brass, one of the most important of the non-ferrous alloys, is an alloy of copper and zinc usually containing small amounts of tin, lead, and iron, and sometimes very small quantities of other elements as well. The percentages of the important constituents usually fall within the following limits:

Cu	Zn	Sn	Pb	Fe
50–90	20–40	0–6	0–2	0–3

Outline of procedure.

One portion of sample is generally used for the entire analysis (determination of copper, zinc, tin, lead, and iron). The alloy is treated with nitric acid to bring copper, zinc, etc. into solution and precipitate tin as hydrous stannic oxide; the latter is filtered off, ignited to stannic oxide, and weighed as such. The filtrate from the tin precipitate is treated with sulfuric acid and evaporated to fumes to expel nitric acid; the residual liquid is taken up in water. Lead sulfate remains undissolved and is filtered off and weighed after ignition at a low temperature. The filtrate from the lead sulfate precipitate is electrolyzed to deposit copper on the cathode, leaving iron and zinc in solution. Alternatively, copper can be precipitated and separated from the latter metals as cuprous thiocyanate. The solution from which copper has been separated is treated with bromine to oxidize iron to the ferric condition, and this metal is then separated from zinc by double precipitation with ammonium hydroxide; the hydrous ferric oxide precipitate is ignited to ferric oxide and so weighed. Finally, zinc is precipitated as zinc ammonium phosphate, and weighed as zinc pyrophosphate after ignition of the precipitate.

Tin.

When an alloy containing tin is treated with nitric acid, there is formed a precipitate of hydrous stannic oxide, the formula of which may be written H_2SnO_3 (metastannic acid) for simplicity:

$$3\ Sn + 4\ HNO_3 + H_2O \rightarrow 3\ H_2SnO_3 + 4\ NO.$$

If nitric acid is the only acid present, the separation of tin is quantitative, and it is not necessary to evaporate to dryness provided the solution is heated and sufficient time is allowed to elapse before filtration (contrast the behavior of hydrous silica, p. 400). Indeed, evaporation should be avoided, because the contamination of the precipitate is then increased. Hydrous stannic oxide is a colloidal precipitate and displays strong adsorptive powers for certain ions. In the analysis of brass, the coprecipitation of copper, lead, and iron with the tin precipitate have to be considered; iron is especially likely to be carried down.[1] In highly exact work the ignited tin residue should be examined for foreign metals as indicated in a subsequent note.

Since the precipitate is colloidal, it is advantageous to use paper pulp (p. 185) in the filtration. The ignition of the precipitate,

$$H_2SnO_3 \rightarrow SnO_2 + H_2O,$$

should be carried out under oxidizing conditions to prevent the reduction of the oxide to the metal; accordingly the carbon of the paper should be burned off at as low a temperature as possible, and the flame gases must be excluded from the crucible. A rather high ignition temperature is required to dehydrate stannic oxide.

Procedure. Since the borings or turnings of brass are likely to be oily, wash the sample with ether, benzene, or similar organic solvent on filter paper, and then dry by exposing to the air on a watch glass for a short time.

Weigh out 1 g. portions into small beakers, add 15 ml. of concentrated nitric acid mixed with 10 ml. of water (keep beaker covered), and evaporate at a temperature of 80° to 100° to a volume of 5 to 10 ml. but not to dryness. This digestion should be extended over a period of at least one hour to insure the quantitative separation of the tin.[2] Then dilute with water to 50 ml., heat to 90° to 100°, and keep at this temperature for ten to fifteen minutes. If the precipitate appears large in amount, stir in a little filter-paper pulp (p. 185). Filter hot through a dense filter paper, receiving the filtrate in a small beaker. If the filtrate is not clear, refilter it; and add more paper pulp if the precipitate persists in running through.

Wash the precipitate at least ten times with hot 1 : 20 nitric acid. Place the paper and its contents in a weighed porcelain crucible, dry and char the filter at as low a temperature as possible, and then ignite strongly for one-half hour over a Meker burner under good oxidizing conditions or in a muffle furnace at 1100°. The flame must not be allowed to envelop the crucible; the crucible should be placed in a slanting position, preferably in an asbestos shield, and left uncovered. Repeat the ignition to constant weight. The ignited residue may be brownish owing to the presence of ferric oxide; it should not be dark gray, for this points to the presence of appreciable amounts of cupric oxide as the result of incomplete washing.

Calculate the percentage of tin in the sample.

NOTE:

The results obtained for tin by the above procedure are slightly high owing to the presence, as already mentioned, of small amounts of iron, copper, zinc, and possibly lead in the ignited residue. The weight of the foreign oxides present can be determined and a correction applied by proceeding in the following way.[1] Mix the residue with about fifteen times its weight of ammonium iodide, and heat at 425° to 475° in a muffle furnace until fumes cease to come off (about 15 minutes). Tin is thus volatilized as stannic iodide, but the other metals remain. Cool and add 2 ml. of nitric acid to the residue. Evaporate to dryness and ignite at low redness. Subtract the weight of the residue from the weight of the impure stannic oxide to obtain the true weight of the oxide. If antimony is present, it is volatilized with the tin.

---

[1] Willard and Furman, *Elementary Quantitative Analysis.*

[2] If no precipitate has appeared at the end of this period, no appreciable amounts of tin are present.

Lead.

Either of the following two methods may be used for the determination of lead in brass:

1. *Determination of lead as sulfate.* The solubility of lead sulfate in sulfuric acid of proper concentration[2] is sufficiently small to permit the quantitative separation of lead as sulfate from many other metals whose sulfates are soluble, including copper and zinc. Other acids such as hydrochloric and nitric must be absent, for they increase the solubility of lead sulfate; they are easily volatilized by heating the solution to fumes of sulfur trioxide after adding sulfuric acid.

The precipitate of lead sulfate is washed with dilute sulfuric acid to minimize solubility losses. The washed precipitate is ignited in a filter crucible at 500°–600°. The precipitate is not collected in paper, because the latter would partially reduce the lead sulfate during the ignition. Above 700° lead sulfate begins to lose sulfur trioxide.

Procedure. Add 4 ml. of concentrated sulfuric acid to the filtrate from the tin precipitate and evaporate on the hot plate to fumes of sulfuric acid. Cool, wash down the sides of the beaker, and again evaporate to fumes to insure the complete expulsion of nitric acid; do not carry the evaporation far past the fuming point. Cool, dilute with 25 ml. of water, heat nearly to boiling, and stir until everything except lead sulfate has gone into solution. Then add 50 ml. of water and allow to stand for at least one hour, stirring occasionally. The liquid must be at room temperature at the end.

Filter off the precipitate in a weighed Gooch or porcelain filter crucible and wash thoroughly with cold 1 : 20 sulfuric acid. Reserve the filtrate and washings. Ignite the precipitate to constant weight at 500° to 600°

---

[1] E. R. Caley and G. Burford, Ind. Eng. Chem., Anal. Ed. *8*, 114 (1936).

[2] H. D. Crockford and D. J. Brawley, J. Am. Chem. Soc. *56*, 2600 (1934), give the following values for the solubility of lead sulfate in sulfuric acid solutions of various concentrations at 25° (only a few of these authors' figures are given here):

CONCENTRATION OF SULFURIC ACID PERCENTAGE BY WEIGHT	MILLIGRAMS $PbSO_4$ IN 100 ML.
1	0.22
5	0.20
10	0.16
20	0.12
30	0.12
40	0.12
50	0.12
60	0.12

Above a concentration of 60 per cent of sulfuric acid, the solubility of lead sulfate increases. At 20°, 100 ml. of water dissolve 4.6 mg. of lead sulfate.

in a muffle or over a flame. In the latter case the filter crucible should be placed in an ordinary porcelain crucible and the latter heated to a barely visible red at the bottom; care should be taken to exclude the reducing flame gases from the crucible. Calculate the percentage of lead.

2. *Electrolytic determination of lead as dioxide.* By electrolysis in nitric acid solution lead can be separated as lead dioxide on the anode (p. 142). The solution must be quite strongly acid with nitric acid, or else some of the lead may be deposited on the cathode; a concentration of 10 ml. of concentrated nitric acid in 100 ml. is sufficiently great. Among the elements that interfere by contaminating the deposit are: manganese, silver, bismuth, antimony, and tin. Arsenic, mercury, and phosphate prevent or hinder complete deposition; chloride, of course, is very objectionable.

The electro-deposited lead dioxide does not have quite the theoretical composition — it weighs more than it should. When the deposit is dried at 120°, the factor used for calculating the weight of lead is 0.864 instead of the theoretical $\frac{Pb}{PbO_2} = 0.8660$. As long as the weight of lead is small, the slight uncertainty regarding the value of the factor is immaterial. The electrolytic method is generally less accurate than the sulfate method.

Procedure. To the filtrate from the metastannic acid (which should not have a volume greater than 100 ml.) add nitric acid in the approximate ratio of 1.5 ml. of the concentrated acid to 10 ml. of solution, and 0.5 ml. of sulfuric acid (to make the deposit more adherent). Connect a clean weighed platinum-gauze electrode (preferably sand-blasted) to the positive terminal of the source of current. A stout platinum wire placed within the gauze serves satisfactorily as the cathode. When all is in readiness, bring the 150 ml. beaker containing the solution beneath the electrodes, and adjust its height so that the electrodes extend very nearly to the bottom and the anode is at least two-thirds immersed. Turn on the current, and adjust the resistances to give 1.5 to 2 amperes at 2 volts or more. Electrolyze for an hour or an hour and a half. Test for completeness of deposition by adding a little water and noting whether any deposit is formed on the freshly immersed gauze or stem of the anode when the electrolysis is continued for fifteen minutes. When deposition is complete, lower the beaker slowly, or raise the electrodes while rinsing off the latter thoroughly with the aid of the wash bottle, taking care that there is no loss of solution. When the electrodes are out of the solution, turn off the current. Dip the gauze anode into water in a beaker, and then rinse with acetone to remove water. Dry the anode with its deposit of lead dioxide in an oven at 120° for one-half hour, cool, and weigh. From the weight of lead dioxide calculate the percentage of lead, using the value 0.864 for the factor $\frac{Pb}{PbO_2}$. Clean the anode as described on page 422.

The cathode may have a deposit of copper. If this is the case, place it in the electrolyzed solution, and let it stand therein until all the copper has been dissolved off. Then remove the cathode, rinse it with water, and reserve the solution in the electrolytic beaker for the determination of copper.

NOTE:

The solution should never contain more than 0.1 gram of lead. With large amounts of lead it often happens that some of the lead dioxide falls off the electrode. It is better to electrolyze overnight with an amperage of 0.5 or slightly less than to use a greater current over a shorter period of time.

Copper.

Either of the two following methods may be used for the determination of copper.

1. ***Electrolytic determination of copper.*** The electrolytic deposition of copper has already been discussed (p. 423). The method is an excellent one for the separation of copper from zinc.

Procedure. If lead was separated by the sulfate method, concentrate the solution to 100 ml. if necessary, add 5 ml. of concentrated ammonium hydroxide to reduce the acidity and 2 ml. of nitric acid to guarantee the formation of a good copper deposit. Electrolyze as described on page 424, keeping the voltage below 2.5 if the solution is not stirred.

If lead was determined electrolytically, it is first necessary to remove the large amount of nitric acid present. Add 3 ml. of concentrated sulfuric acid to the solution from which lead has been deposited electrolytically and evaporate until fumes of sulfur trioxide appear. Cool, dilute with water to 75 or 100 ml., add 2 ml. of concentrated nitric acid, and electrolyze out the copper as directed on page 424. Calculate the percentage of copper.

2. ***Determination of copper by precipitation as cuprous thiocyanate.*** Copper can be precipitated quantitatively as cuprous thiocyanate in feebly acid solution by an alkali thiocyanate in the presence of a reducing agent such as sulfurous acid:

$$2\,Cu^{++} + 2\,CNS^- + SO_3^= + H_2O \rightarrow 2\,CuCNS + SO_4^= + 2\,H^+.$$

The solution must not be more than slightly acid, because the solubility of the precipitate is otherwise too great, and should not contain oxidizing agents such as nitric acid. An excess of thiocyanate is required for quantitative precipitation, but this excess must not be too large (less than $0.05\ N$), for the solubility increases as the result of complex formation.[1] For washing the precipitate, a solution of ammonium thiocyanate containing a little sulfurous acid is used, followed by 20 per cent alcohol if the precipitate is to be weighed as thiocyanate. Cuprous thiocyanate can be weighed as such after heating to 105° to 120°; above 160° the precipitate decomposes. The precipitate may also be converted into cupric oxide by igniting strongly in a non-reducing atmosphere; it can also be determined volumetrically, e.g., titration with potassium iodate in a solution of proper acidity. Common metals that interfere are lead, mercury, and silver. Most other metals are without effect. Excessive amounts of ammonium salts are undesirable.

Procedure. If the electrolytic method was used for lead, nitric acid must first be removed from the solution containing the copper. Add 3 ml.

---

[1] I. M. Kolthoff and G. H. P. v. d. Meene, Z. anal. Chem. *72*, 337 (1927).

of concentrated sulfuric acid to the solution from which lead has been removed electrolytically, and evaporate until dense fumes of sulfur trioxide appear. Cool, add 50 ml. of water, and stir to dissolve the separated solids. Add dilute ammonium hydroxide slowly to the solution until a faint precipitate is obtained, signifying the neutralization of the acid, add 10 ml. of 1 : 5 sulfuric acid, dilute to 300 ml., and then add 25 ml. of a 5 per cent solution of ammonium or sodium bisulfite. Heat nearly to boiling, and add slowly with stirring 15 ml. of a 10 per cent solution of ammonium thiocyanate. Allow the solution to cool to room temperature over a period of one or two hours. Then filter through a filter crucible (Gooch, sintered-glass, or porous porcelain), and wash the precipitate with a cold solution containing 0.1 per cent of ammonium thiocyanate and 0.01 per cent of ammonium bisulfite. Ten washings should suffice. Reserve the filtrate and washings for the determination of iron and zinc. Finally wash the precipitate with 20 per cent alcohol to remove ammonium thiocyanate; reject these washings. Dry the precipitate to constant weight at 105° to 120° and weigh as CuCNS. Calculate the percentage of copper.

Iron.

The separation of iron from zinc in the analysis of brass is usually effected by precipitating the former as the hydrous oxide with ammonium hydroxide after the oxidation of the metal to the ferric condition, and the destruction of thiocyanate and sulfite (if the thiocyanate method was used for copper) by evaporation with nitric acid and hydrochloric acid. It has already been mentioned (p. 320) that zinc is coprecipitated with hydrous ferric oxide. The use of an excess of ammonium hydroxide and ammonium chloride improves the separation. The amount of iron present in brass is usually so small that generally not more than one reprecipitation of the iron need be made. Any aluminum present will be partially precipitated with the iron and weighed with the ignited ferric oxide, and the remainder will be precipitated with the zinc ammonium phosphate in the determination of zinc.

Procedure. If the copper was separated electrolytically, heat the solution from the electrolysis (p. 701) to boiling, add 2 or 3 ml. of saturated bromine water, and proceed as directed in the next paragraph. If the thiocyanate method was used for copper, add 40 ml. of concentrated nitric acid and 20 ml. of concentrated hydrochloric acid to the filtrate from the cuprous thiocyanate precipitate, and evaporate practically to dryness; add 4 ml. of concentrated hydrochloric acid, warm to dissolve the residue, and dilute to 75 ml. with water. If there is a precipitate (silica), filter it off on a small paper, wash with 1 : 100 hydrochloric acid, and treat the filtrate as described below; reject the precipitate.

Heat the solution containing the iron and zinc nearly to boiling, add concentrated ammonium hydroxide until a permanent precipitate is obtained, and then 10 ml. in excess. Allow the precipitate to settle, filter it off on a small paper, and wash three or four times with 1 : 100 ammonium hydroxide. Replace the beaker containing the filtrate and washings with the precipitation beaker, and pour 20 ml. of hot 1 : 3 hydrochloric acid through the filter to dissolve all the precipitate. Wash the paper with hot

1 : 100 hydrochloric acid and then with water to remove acid. Precipitate the iron as before, using a 5 ml. excess of ammonium hydroxide. Collect the precipitate in the same filter as before, and wash it thoroughly with the ammonium hydroxide wash solution, receiving the filtrate and washings in the beaker containing the first filtrate. Reserve the combined filtrates for the determination of zinc. Ignite the precipitate to ferric oxide (p. 322) and weigh. Calculate the percentage of iron.

Zinc.

Under the proper conditions zinc can be precipitated quantitatively as zinc ammonium phosphate, $ZnNH_4PO_4 \cdot 6\ H_2O$.

The precipitate is soluble in acid and basic solutions but possesses only a slight solubility in solutions having a pH ranging from 5.5 to 7 (p. 373). The precipitant used is diammonium hydrogen phosphate (not ammonium dihydrogen phosphate). The hydrogen ions liberated in the precipitation react with the excess diammonium hydrogen phosphate to give the dihydrogen phosphate, and the pH of the mixture is kept within the permissible limits. The precipitate which is first formed is actually zinc phosphate; this flocculent precipitate is rapidly transformed into the crystalline double phosphate on standing in the precipitation liquid. Zinc ammonium phosphate may be washed with a dilute solution of diammonium phosphate and finally with 50 per cent neutral alcohol to remove the ammonium phosphate. On ignition the precipitate is converted into the pyrophosphate, $Zn_2P_2O_7$.

Zinc, being one of the principal constituents of brass, is sometimes reported by difference.

Procedure. If copper was determined as thiocyanate, proceed with the filtrate from the iron separation as directed in the next paragraph. If lead and copper were determined electrolytically, it is advisable to remove the excessive amounts of ammonium salts present by destroying them with nitric and hydrochloric acids. Therefore in this case add approximately 25 ml. each of concentrated hydrochloric and nitric acids to the filtrate from the hydrous ferric oxide precipitate and evaporate to dryness or to fumes of sulfur trioxide. Add 2 or 3 ml. of strong hydrochloric acid, warm, dilute with water to 50 ml., and filter off any insoluble silica that may be present.

Adjust the volume of the zinc solution to 150 to 200 ml. by dilution or evaporation as the case may be; add a few drops of methyl red and then ammonium hydroxide carefully until the solution becomes yellow. Heat the solution just short of boiling, and slowly add 30 ml. of a freshly prepared 20 per cent solution of diammonium hydrogen phosphate.[1] Keep the solution hot for one-half hour by setting the beaker on the steam bath. At the end of this time the precipitate should be crystalline and should settle readily when stirred up. The solution should be yellow in color, not pink. Then remove the beaker from the heat and allow to stand for one to two hours. Filter through a Gooch or porous porcelain filter crucible, and wash the precipitate with a 1 per cent diammonium phosphate solution (prepared by diluting the precipitating solution) until it is chloride-free. Finally wash with a neutral 50 per cent solution of alcohol to remove the ammonium phosphate. Dry the precipitate at a low temperature, and then gradually heat to 900° to 1000° in a muffle furnace; repeat the ignition until constant weight is attained. In the absence of a muffle, a Meker burner may be used for the heating. In this case place the filter crucible in an ordinary porcelain crucible and take every precaution to prevent the entrance of the flame gases which would reduce the precipitate. From the weight of zinc pyrophosphate obtained, calculate the percentage of zinc.

---

[1] This solution should give a very faint pink with phenolphthalein; if it does not, add ammonium hydroxide until a barely perceptible color appears.

Sum up the percentages of tin, lead, copper, iron, and zinc.

REFERENCES ON THE ANALYSIS OF NON-FERROUS ALLOYS

American Society for Testing Materials, *A.S.T.M. Methods of Chemical Analysis of Metals*, A.S.T.M., Philadelphia, 1936.

H. V. Churchill and R. W. Bridges, *Chemical Analysis of Aluminum*, Aluminum Research Laboratories, New Kensington, Pa., 1941.

E. Gregory and W. W. Stevenson, *Chemical Analysis of Metals and Alloys*, Blackie and Son, London, 1937.

F. Ibbotson and L. Aitcheson, *Analysis of Non-Ferrous Alloys*, Longmans, Green and Co., 1922.

W. A. Naish and J. E. Clennell, *Selected Methods of Metallurgical Analysis*, John Wiley and Sons, New York, 1929.

W. B. Price and R. K. Meade, *The Technical Analysis of Brass and Non-Ferrous Alloys*, John Wiley and Sons, New York, 1922.

CHAPTER XLIV

ANALYSIS OF STEEL

The analysis of iron and steel occupies an important place in the field of practical analysis, and the analyst is often called upon to make a chemical examination of these materials. The properties of a ferrous material are determined by the kinds and amounts of elements other than iron that are present. It is these subsidiary elements that are determined in the analysis of the metal; iron itself is rarely determined in irons or steels.

The elements that must be considered in the analysis of irons and steels fall into three classes. The first group contains the elements that are always present: (iron), carbon, manganese, phosphorus, sulfur, and silicon. These are very frequently determined, because they influence the properties of the metal, and the limits of a number of them are usually specified in the purchase and sale of the material. The second group of elements comprises the common alloying elements: copper, nickel, chromium, vanadium, molybdenum, tungsten, and cobalt. The third group includes elements, usually occurring in small amounts, that do not have any very pronounced effect on the properties of the product; these are sometimes added intentionally (deoxidizers) or are introduced in the raw materials. Among these may be named aluminum, titanium, arsenic, tin, antimony, and zinc. Included in this group also are zirconium, tantalum, and other elements added to the steel for experimental purposes.

Generally, a number of methods are available for the determination of each element. The method adopted will depend upon the end in view. Some methods are much more accurate than others; but these, nearly without exception, require a longer time for execution. Both the exact and the more rapid, less accurate methods have their place. In a works laboratory where a sample must be analyzed quickly to furnish information respecting the mixing of charges, the disposition, or modification of a product, highly accurate methods need not be used; a more rapid method may give an accuracy satisfactory for the purpose. On the other hand, when the finished product is sold, the need for accurate methods makes itself felt. The suitability of a ferrous material for the intended purpose will depend upon the exact amounts of subsidiary elements present, and it will be necessary to determine them with great accuracy. Both the manufacturer who guarantees the product and the purchaser who buys on specifications require accurate analyses.

In the following, stress will be laid chiefly upon the exact methods of determining a number of important elements found in steel and iron. The chapter is in no sense complete, since some elements are not considered at all. For a detailed treatment of the subject, the student is referred to special works on iron and steel analysis (see the list on p. 730, Lundell, Hoffman, and Bright's *Chemical Analysis of Iron and Steel* is especially recommended).

The directions as given in the procedures for the determination of manganese, phosphorus, sulfur, and silicon apply to plain carbon steels but may often be used for alloy steels as well. The possibility of interference by other elements must always be borne in mind. It is assumed that a representative sample is taken for analysis; otherwise the results may be of no value or, what is worse, may be misleading.

Carbon.

Carbon may exist combined or free in ferrous products. In most steels the element occurs combined as carbides, whereas in cast iron it exists uncombined in the form of graphite. The sum of combined and uncombined carbon is known as total carbon, and the determination of this is of great technical importance.

Determination of total carbon.

Method. The sample of ferrous material is burned in a stream of pure oxygen at a temperature of 1000° or above, and the carbon dioxide formed is caught in an absorbent such as ascarite (asbestos impregnated with sodium hydroxide). From the gain in weight of the absorbent, the amount of carbon present is calculated.

Apparatus. A simple assembly for the determination of carbon by combustion is shown in Figure 129. The train represented is typical of those commonly used. Naturally, installations will vary from case to case in various details, to suit particular needs.

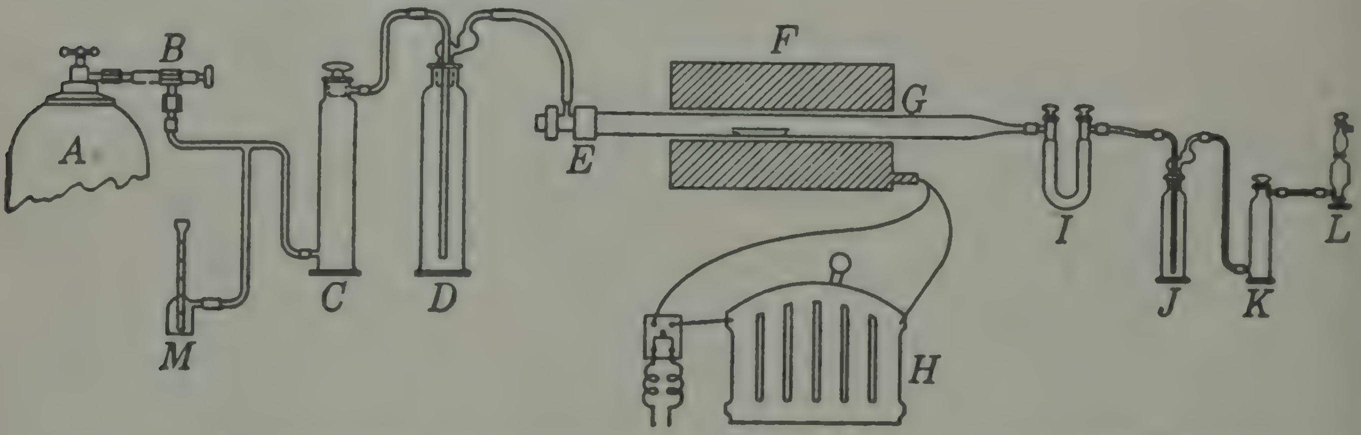


FIG. 129. Apparatus for determination of carbon in steel by combustion.

In Figure 129, *A* is a tank of commercial oxygen (purity greater than 99 per cent and free from organic matter) with a reducing valve *B*, and *M* is a mercury pressure gauge and safety valve. *C* is a tower filled with ascarite, the purpose of which is to absorb any carbon dioxide in the oxygen. The wash bottle *D* contains concentrated sulfuric acid and is connected to the combustion tube *G* through a breech connector *E*. A one-hole rubber stopper can be substituted for the breech connector; the stopper should be protected on the inside from radiant heat by a perforated asbestos disk or plug.

The combustion tube may be made of porcelain, sillimanite, vitrified clay, or silica, the first usually being employed. The length of this tube may conveniently be 50 or 60 cm. The inside diameter should be approximately 2.5 cm. The exit end of the combustion tube should preferably be tapered to permit it to be connected directly to the train following. The electric furnace *F* for heating the combustion tube should be approximately 30 cm. in length and should be capable of giving a temperature of 1000° to 1100°. The rheostat *H* permits the temperature to be regulated. A thermocouple should be used to find the setting of the rheostat which gives the required temperature for combustion (usually 1000°).

The boat in which the sample is burned may be of nickel (low in carbon), vitrified clay, alundum, quartz, or porcelain; boats of the first three materials are most often used. The boat should be provided with a special slotted cover to prevent damage to the combustion tube by spattering molten iron oxide. Before a nickel boat is used, it should be heated to 1000° in oxygen. To protect the boat from the molten oxide, it is lined with an inert infusible material such as alundum (aluminum oxide).

The exit end of the combustion tube is connected to a tower or U-tube *I* packed with asbestos, the function of which is to screen out finely divided iron oxide and sulfur trioxide. The wash bottle *J* contains concentrated sulfuric acid saturated with chromic acid. Here the sulfur dioxide in the gas stream is oxidized to sulfur trioxide, which is retained in the liquid and in the next tube.[1] The tube *K* is filled with a good desiccant, preferably anhydrous magnesium perchlorate (anhydrone).[2]

L is the carbon dioxide absorption bulb. This may have a variety of forms, as shown in Figure 130. The best absorber for the carbon dioxide is soda-asbestos, ascarite, which can be purchased. Soda-lime may be used instead as an absorber. The carbon dioxide absorbent is covered on the exit side with a layer of desiccant which should be the same as the one used in the tube *K*, in order that there may be neither loss nor gain of moisture. Water is formed when carbon dioxide reacts with sodium hydroxide, and the ascarite cannot be relied upon to retain this moisture completely. The absorption bulb should be weighed against a like tube used as counterpoise, and it must naturally be filled with oxygen. Generally, it is not necessary to use a protecting tube for *L*.

Procedure (for plain carbon steels containing less than 0.1 per cent of sulfur).[3] Assemble the apparatus as described in the preceding section and see that the train is gas-tight.

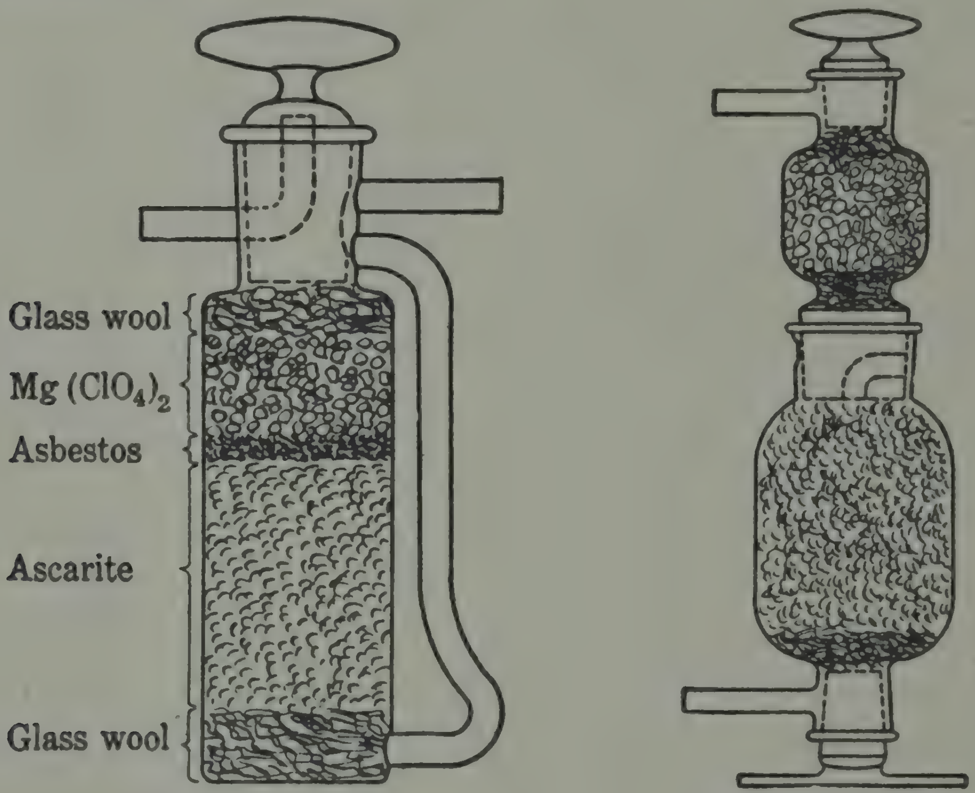
A blank and a standard sample should be run before carbon is determined in the unknown. To run a blank, proceed as follows. Place the covered boat with its lining of alkali-free alundum (90-mesh) in the hot zone of the combustion tube and heat the furnace to 1000°. Pass a stream of oxygen through the tube at the rate of about 100 ml. per minute for fifteen minutes while the train is disconnected at *L* (Fig. 129). Then connect in the rest of the train and pass oxygen through at the same rate for about five minutes. Close the absorption vessel *L*, disconnect it, and allow it to stand near the balance for ten minutes. Then weigh (opening the vessel momentarily to equalize the pressure), using a similar tube as tare. Replace *L* in the train and pass oxygen through the system (combustion tube at 1000°) at the rate of about 200 ml. per minute for ten minutes. Turn off the oxygen, close the absorption tube, disconnect it, and weigh after it has stood in or near the balance case for ten minutes. Make another blank determination as before and compare the two results. The increase in weight in either blank should not exceed 1 mg. in the usual case, and the agreement should be within 0.5 mg. If satisfactory agreement is not obtained, repeat the blank determination until the gain in weight is constant.

---

[1] For ferrous materials containing more than about 0.1 per cent of sulfur, the sulfuric acid saturated with chromic acid is replaced by a 50 per cent aqueous chromic acid solution.

[2] Magnesium perchlorate trihydrate (dehydrite) is also satisfactory, especially in routine work. Calcium chloride is undesirable as a desiccant because it may retain carbon dioxide (p. 384).

[3] The conditions specified in this procedure are essentially those recommended by Lundell, Hoffman, and Bright, *Chemical Analysis of Iron and Steel*, p. 170.



Nesbitt bulb Fleming bulb

FIG. 130. Absorption vessels for carbon dioxide.

When a satisfactory blank has been obtained, weigh 2 to 3 g. of a standard sample (i.e., one with a known content of carbon) into the boat, placing the steel in the furrow made in the alundum lining. The sample should be in the form of small shavings or chips, and these should be closely packed in the groove of alundum. Disconnect the train at the entrance end of *G*, and push the covered boat into the center of the combustion tube, which should be at 1000°. Close the tube, open the absorption vessel *L*, and after one-half to one minute pass in oxygen rapidly at the rate of 300 to 400 ml. per minute while the sample is burning. When the combustion is complete (after two or three minutes), decrease the oxygen current to approximately 200 ml. per minute, and continue it at this rate for five minutes to sweep out all the carbon dioxide. Then turn off the oxygen, close the absorption tube, remove it from the train, and place it near the balance. After fifteen minutes (when it should be at room temperature), open the tube momentarily and weigh it against the tare. Examine the residue in the boat; if there is any evidence of incomplete combustion, reject the result. Otherwise, calculate the percentage of carbon in the standard sample, subtracting the blank correction. If a satisfactory check is obtained with the percentage of carbon known to be present, run the unknown sample in exactly the same way as described above. Report the percentage of carbon in the unknown.

Manganese.

1. *Bismuthate method.*[1]

Method. The steel is dissolved in nitric acid, and manganese is oxidized to permanganate in cold solution with sodium bismuthate:

$$2\,Mn^{++} + 5\,NaBiO_3 + 14\,H^+ \rightarrow 2\,MnO_4^- + 5\,Na^+ + 5\,Bi^{+++} + 7\,H_2O.$$

The excess bismuthate is filtered off, and a measured excess of ferrous sulfate is added to the filtrate to reduce permanganate to manganous salt:

$$MnO_4^- + 5\,Fe^{++} + 8\,H^+ \rightarrow Mn^{++} + 5\,Fe^{+++} + 4\,H_2O.$$

The excess of ferrous iron is then determined by titration with standard potassium permanganate solution (p. 595).

The oxidation of manganese by sodium bismuthate can be carried out in nitric or sulfuric acid solution. The acidity must be regulated, the concentration of manganese must not be too high, and a sufficient excess of bismuthate must be added to obtain correct results. Hydrochloric and hydrofluoric acids must be absent; moderate amounts of phosphoric acid do not interfere. The nitric acid used in the procedure must be free from nitrous acid. The method is not applicable to samples containing cobalt and cerium. The presence of chromium and vanadium is undesirable; but, by adopting certain precautions, satisfactory results can be obtained when not too large amounts of these are present. Sodium bismuthate will oxidize chromium to some extent; moreover, the permanganate formed will oxidize chromium slightly. The speed of both these reactions is decreased by cooling the solution, so that by working without undue slowness in cold solution (10°) satisfactory results can be obtained when 1 per cent or so of chromium is present in the sample. Vanadium interferes slightly, because it is oxidized rather slowly by potassium permanganate after reduction by ferrous sulfate, thus causing a fleeting end point.

This is the most accurate method for manganese.

Procedure.

Reagents: *Sodium bismuthate.* Available oxygen should correspond to at least 75 per cent $NaBiO_3$. Chloride and manganese should be absent.

1 : 30 Nitric acid free from nitrous acid. Boil concentrated nitric acid (hood) for one or two minutes, cool, and dilute with water.

Standard solutions: *Potassium permanganate, 0.03 N.* Dissolve 1 g. of potassium permanganate in 1 liter of water, allow to stand for several days, and filter through asbestos. Keep the permanganate solution in a glass-stoppered bottle. Standardize the solution by weighing out 0.1 g. of pure dried sodium oxalate, dissolving in 100 ml. of hot water containing 15 ml. of 6 *N* (1 : 5) sulfuric acid, and titrating slowly with continuous stirring (p. 592).

---

[1] W. Blum, J. Am. Chem. Soc. *34*, 1395 (1912); G. E. F. Lundell, J. Am. Chem. Soc. *45*, 2600 (1923); T. R. Cunningham and R. W. Coltman, Ind. Eng. Chem. *16*, 58 (1924).

Ferrous ammonium sulfate, 0.03 N. Dissolve 12 g. of $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6\ H_2O$ in 1 liter of 1 : 20 sulfuric acid.

Weigh a 1 g. sample (Mn = 0.3 to 1.0 per cent) into a 250 ml. beaker, and dissolve in 50 ml. of 1 : 3 nitric acid. Boil for a few minutes, remove the beaker from the heat, add 0.5 g. of sodium bismuthate, and again boil for a few minutes. A precipitate of manganese dioxide or a pink color due to permanganate should appear; if neither a precipitate nor a color is produced, add more bismuthate. Then add dropwise a strong solution of sodium sulfite (or sulfurous acid) until the precipitate or permanganate coloration disappears. Boil for four or five minutes. Cool the solution to approximately 15°, and add 0.5–1 g. of sodium bismuthate; some of the reagent should remain undissolved. Stir for one to two minutes, add 50 ml. of cold 1 : 30 nitric acid, and filter through a Gooch crucible (or a sintered-glass crucible) with the aid of suction. Of course bismuthate must not run through the filter. Wash the residue well with dilute nitric acid. Add 3 ml. of 85 per cent phosphoric acid to the filtrate, and slowly run in ferrous ammonium sulfate solution from a buret or pipet until a slight excess is present as indicated by the disappearance of the color due to permanganate. Then titrate the solution with standard permanganate to the first pink tinge (p. 602).

Standardize the ferrous ammonium sulfate solution by running a blank through all the steps of the procedure, taking the same volume of ferrous ammonium sulfate solution as used in the determination itself. Report the percentage of manganese.

NOTES:

1. The solution of the sample is subjected to a preliminary oxidation with sodium bismuthate to destroy any reducing substances present (carbonaceous matter) that might later react slowly with permanganate.

2. The concentration of nitric acid during the oxidation should be at least 10 per cent and preferably 20 per cent by volume. As much as 50 mg. of manganese can be present in 100 ml., and even 100 mg. if the oxidized solution is filtered without undue delay. Approximately 0.25 g. of 80 per cent sodium bismuthate is needed to oxidize 10 mg. of manganese quantitatively.

3. The oxidation can be made at room temperature (up to 25°) in the absence of chromium, but it is best to cool the solution to 10°–15°. The oxidation is complete, if the solution is stirred, in one minute, providing the conditions mentioned above are fulfilled. A longer period of standing does no harm.

4. The residue of sodium bismuthate should be thoroughly washed with dilute nitric acid, because it shows a tendency to retain permanganate, especially if a high concentration is present.

5. The filtrate should not be allowed to stand for any length of time before titration, because the permanganic acid may decompose.

2. *Persulfate-arsenite method.* With silver ions as catalyst, manganous salts can be oxidized to permanganate by alkali persulfates in hot acid solution:

$$2\,Mn^{++} + 5\,S_2O_8^{=} + 8\,H_2O \rightarrow 2\,MnO_4^{-} + 10\,SO_4^{=} + 16\,H^{+}.$$

In the presence of phosphoric acid as much as 100 mg. of manganese can be smoothly oxidized in this way.[1] The permanganate thus formed can be titrated with sodium arsenite solution. The reaction between permanganate and arsenite does not proceed stoichiometrically, and the titer of the latter solution must therefore be found by titrating a known amount of permanganate under the same conditions as the unknown solution. Heptavalent manganese is reduced by arsenite to a valence state approximately represented by $Mn^{+3.3}$, which has a yellow to brown color in solution. The end point of the titration is not very sharp, especially when comparatively large amounts of manganese are present; but the method has the advantage of being a very rapid one. It is also possible to use a solution containing sodium arsenite and sodium nitrite in equivalent amounts for the titration. In this case the permanganate is reduced nearly stoichiometrically to manganous ion (if silver is first precipitated with chloride), and the color change is from pink to colorless at the end point, so that the latter can be found more exactly than when sodium arsenite alone is used. The mixed reducing solution must be standardized against a known amount of manganese oxidized under the same conditions as the sample.

Procedure.[2]

Reagents: (1) *Acid mixture.*

Water	525 ml.
Sulfuric acid, conc. (sp.g. = 1.84)	100 ml.
Phosphoric acid, 85 per cent	125 ml.
Nitric acid, conc. (sp.g. = 1.42)	250 ml.

First add the sulfuric acid to the water, cool, and then add the nitric and phosphoric acids.

(2) *Silver nitrate solution, 0.1 M.*

(3) *Ammonium persulfate solution*, 25 g. (of 95 per cent salt) in 80 ml. of water. Ammonium persulfate slowly decomposes in solution, and therefore this solution should not be kept for more than two or three days.

(4) *Sodium chloride solution, 0.2 M.*

(5) *Sulfuric acid, 12 N.*

Standard solutions: (1) *Sodium arsenite-sodium nitrite, 0.05 N.* Dissolve 1.3 g. of pure As_2O_3 in 25 ml. of 4 *N* sodium hydroxide solution, dilute to 200 ml., add slightly more than enough dilute sulfuric acid to neutralize the hydroxide, and then a slight excess of sodium bicarbonate to neutralize the acid (the solution should finally be neutral to litmus paper). Dissolve 0.85 g. of $NaNO_2$ in the solution thus obtained and dilute to 1 liter.

(2) *Potassium permanganate, 0.05 N.* Prepare and standardize against pure dry sodium oxalate in the usual manner.

Standardization of sodium arsenite-sodium nitrite solution. Pipet 10 ml. of standardized 0.05 *N* potassium permanganate solution into a 250 ml. Erlenmeyer flask, and add 1.0 g. of electrolytic iron of known manganese content and 30 ml. of the sulfuric-phosphoric-nitric acid mixture. Warm to hasten solution, and finally boil for two to three minutes to expel oxides of nitrogen. Then add 50 ml. of cold water, 5 ml. of silver nitrate solution, and 10 ml. of ammonium persulfate solution. Heat to boiling and boil for thirty to forty-five seconds. Immediately cool the flask and its contents to 20° to 25° by placing in water. Add 5 ml. of sodium chloride solution and 10 ml. of 12 N sulfuric acid. Then titrate with arsenite-nitrite solution. Run in the reducing solution at a uniform rate not exceeding 5 or 6 ml. per minute, swirling the liquid in the flask continuously, until the solution has become pale pink, and then continue the addition more slowly, allowing about five seconds between drops. When very near the end point, as indicated by the very pale pink color, allow approximately ten seconds between drops or fractions of a drop. This slow addition is required only for the last few drops. The end point is reached when the color changes abruptly to white (suspended silver chloride). If the titration has been correctly performed, a drop of 0.05 N permanganate solution added after the end point has been reached will give a coloration persisting for at least three minutes.

---

[1] H. A. Bright and C. P. Larabee, Bur. Standards J. Research *3*, 573 (1929).

[2] E. B. Sandell, I. M. Kolthoff, and J. J. Lingane, Ind. Eng. Chem., Anal. Ed. *7*, 256 (1935).

Determination. Dissolve a 0.9 to 1.1 g. sample of steel in 30 ml. of the acid mixture, and then proceed as directed in the standardization (beginning with the second sentence).

NOTES:

1. If an accuracy greater than ± 0.01 per cent of manganese is not required, the addition of iron in the standardization may be omitted. Then standardize as follows: Transfer 30 ml. of acid mixture to a 250 ml. Erlenmeyer flask and add 50 ml. of water, 1 ml. of silver nitrate solution, and 10 ml. of ammonium persulfate solution. Boil for one minute, cool to room temperature, add 10 ml. of 0.05 N standard potassium permanganate, and titrate with the arsenite-nitrite solution as described in the preceding.

2. An equivalent amount of pure ferrous or ferric sulfate (but not ferrous ammonium sulfate or ferric alum) as free as possible from manganese may be used instead of electrolytic iron in the standardization. In any case, the manganese content of the iron or iron salt added must be determined colorimetrically, preferably with periodate as reagent (see colorimetric method below), and a correction applied if necessary.

3. When the manganese content of the sample falls outside the range 0.3 to 0.8 per cent (using a 1 g. sample), the arsenite-nitrite solution should be standardized against a volume of standard potassium permanganate that contains roughly the same quantity of manganese as the sample. Not more than 15 mg. of manganese may be present in the solution when diluted to 100 ml. previous to titration. In other words, using a 1 g. sample, not more than 1.5 per cent of manganese may be present in the material analyzed if the above directions are to be followed.

4. Alloying elements such as chromium, vanadium, nickel, and molybdenum do not interfere when present in the usual amounts, except that the end point is less sharp when the solution is colored.

5. Cast irons may be analyzed by the above procedure if the graphite, left after dissolving the sample, is filtered off before the oxidation.

3. ***Colorimetric method.*** This method is most suitable for small quantities of manganese; it is based upon the oxidation of manganese to permanganate and the comparison of the color of the solution with that of another containing a known amount of manganese present as permanganate. Sodium bismuthate, persulfate with silver nitrate, and potassium periodate are some of the oxidizing agents that can be used. The last reagent[1] is to be recommended. In hot acid solution, periodate oxidizes manganese to permanganate according to the following equation:

$$2\,Mn^{++} + 5\,IO_4^- + 3\,H_2O \rightarrow 2\,MnO_4^- + 5\,IO_3^- + 6\,H^+.$$

Phosphoric acid must be present in the solution to prevent the precipitation of ferric periodate and iodate, and to decolorize ferric iron (complex formation).

Procedure. Dissolve 0.5 to 1.0 g. of steel in 50 ml. of 1 : 3 nitric acid and boil for one or two minutes to expel oxides of nitrogen. Add carefully approximately 1 g. of ammonium persulfate and boil for ten to fifteen minutes to oxidize carbon compounds and to destroy the excess of persulfate. If manganese oxides separate or a color of permanganate is visible, add a few drops of sulfurous acid or sodium sulfite solution to reduce the manganese and render the solution clear, and boil for a few minutes to expel the excess of sulfur dioxide. Dilute the solution to approximately 100 ml., add 5 to 10 ml. of 85 per cent phosphoric acid and 0.5 g. of potassium periodate, and boil for three minutes. Cool the solution and make up to 250 ml. With the aid of a colorimeter compare the color of the unknown solution with that of a solution containing a known similar amount of manganese treated in the same way. It is best to use a Bureau of Standards sample of steel to furnish a solution of known manganese content. If such samples are not available, take a suitable volume of standardized potassium permanganate solution, add 50 ml. of 1 : 3 nitric acid, reduce the permanganate by adding a little sulfite, boil to expel sulfur dioxide, and proceed as above.

NOTES:

1. The manganese content of a solution for colorimetric comparison should not exceed 2 mg. per 100 ml.

2. The presence of metals such as chromium and nickel that impart a color to the solution must be corrected for by adding approximately the same amounts to the comparison solution.

3. Solutions of permanganate containing an excess of periodate are stable indefinitely.

Phosphorus.

Phosphorus exists in steel in the form of phosphide, and it must be oxidized to orthophosphate before it can be determined. For this reason nitric acid is used to dissolve the sample (a nonoxidizing acid would cause loss of phosphorus as phosphine), and the oxidation is completed with potassium permanganate. Ammonium molybdate is then added to precipitate ammonium phosphomolybdate, $(NH_4)_3PO_4 \cdot 12\ MoO_3 \cdot 2\ HNO_3 \cdot H_2O$. The precipitate thus obtained can be treated in a number of ways to determine phosphorus, some of which are:

---

[1] H. H. Willard and L. H. Greathouse, J. Am. Chem. Soc. *39*, 2366 (1917).

1. Solution in ammonium hydroxide, and precipitation of magnesium ammonium phosphate from this solution by the addition of magnesia mixture, followed by ignition to magnesium pyrophosphate (p. 390).

2. (a) Drying at 110° and weighing as $(NH_4)_3PO_4 \cdot 12\ MoO_3$ (p. 396); (b) heating to 450° and weighing as $P_2O_5 \cdot 24\ MoO_3$ (p. 396).

3. Dissolving in a measured volume of standard base and titrating the excess of the latter with standard acid.

1. *Magnesia method.* This method for phosphorus has already been considered at length in Chapter XXIV.

Procedure.

Reagents: *Ammonium molybdate reagent.* Make up two solutions:

(1) Dissolve 100 g. of ammonium molybdate in a mixture of 400 ml. of water and 80 ml. of concentrated ammonium hydroxide.

(2) Dilute 400 ml. of concentrated nitric acid with 600 ml. of water. Immediately before use, slowly pour a suitable volume of solution (1) into twice its volume of solution (2).

Magnesia mixture. Dissolve 50 g. of magnesium chloride hexahydrate and 100 g. of ammonium chloride in 500 ml. of water. Make ammoniacal, let stand overnight, filter off any precipitate formed, make the filtrate very slightly acid with hydrochloric acid, and dilute to 1 liter.

Weigh out 3 g. of steel into a 250 ml. Erlenmeyer flask, add 75 ml. of 6 N (3 : 5) nitric acid, and warm gently to dissolve. Then add 10 ml. of 2 per cent potassium permanganate solution and boil for a few minutes to precipitate manganese dioxide; add more permanganate if no precipitate appears. Dissolve the precipitate by adding dropwise a solution of sodium sulfite. Boil again for a few minutes to expel oxides of nitrogen and sulfur dioxide. Cool the solution to approximately 50°; add 35 ml. of 6 N (3 : 4) ammonium hydroxide[1] and 75 ml. of molybdate reagent. Stopper the flask and shake for five or ten minutes. Wash off the stopper and set the flask aside for at least two hours or, better, overnight.

Filter off the precipitate on a S. and S. No. 589 Blue Band filter paper, wash with 1 : 100 nitric acid two or three times, and then five or six times with 5 per cent ammonium nitrate solution. The filtrate and washings should be mixed and reserved to see if further precipitation of ammonium phosphomolybdate occurs. Dissolve the precipitate in 20 ml. of 6 N ammonium hydroxide containing 2 g. of citric acid, catching the solution in a 250 ml. beaker. Wash the filter paper three or four times with 1 : 20 ammonium hydroxide, then an equal number of times with hot water, and finally a few times with 1 : 20 hydrochloric acid. (If the ammoniacal solution of the precipitate is not clear at this point, see Note 3.) Add a few drops of methyl red, and acidify the solution with hydrochloric acid. Next add 20 ml. of magnesia reagent, cool the solution in ice water, and make alkaline with ammonium hydroxide. Stir for five minutes; or if no precipitate appears, set the solution aside for an hour or so. Finally add 10 ml. of concentrated ammonium hydroxide, and allow the solution to stand overnight in a cool place.

---

[1] On the addition of the ammonia, the solution should turn dark reddish-brown, but no permanent precipitate of hydrous ferric oxide should form (too much ammonia). Add the ammonium hydroxide slowly with shaking.

Filter on paper, and wash the precipitate three times with 1 : 20 ammonium hydroxide. Place the original beaker under the funnel, and dissolve the precipitate in about 20 ml. of 6 *N* hydrochloric acid. Carefully wash the filter paper with hot 6 *N* hydrochloric acid. Add 0.5 to 1 g. of ammonium bromide to the combined filtrate and washings, and boil down the solution to a volume of 5 to 10 ml. but not further. Dilute to 50 to 75 ml.; add 0.1 g. citric acid and 2 to 3 ml. of magnesia reagent. After cooling the solution in ice water, make the liquid ammoniacal, stir, and allow to stand overnight before filtering.

Collect the precipitate on paper. Wash with 1 : 20 ammonium hydroxide, transfer the paper to a crucible, char, and burn off the carbon at the lowest possible temperature. Then ignite to constant weight at 1050° to 1100°. Test the ignited residue for purity by adding 5 ml. of 1 : 1 nitric acid and 20 ml. of water. If there is a residue, filter it off, wash it with hot water, ignite in a platinum crucible, and weigh. Pour a few drops of hydrofluoric acid into the crucible, evaporate to dryness, ignite, and again weigh. Subtract the loss in weight, if any is found, from the weight of the impure magnesium pyrophosphate. Report the percentage of phosphorus.

NOTES:

1. The above procedure is applicable to plain carbon steels and many alloy steels. The directions must be modified for the analysis of cast iron, chrome-vanadium steels, tungsten steels, etc. (cf. p. 393 for interfering substances in the phosphomolybdate precipitation).

2. Citric acid is added to the ammoniacal solution of ammonium phosphomolybdate to prevent the contamination of the magnesium ammonium phosphate precipitate by such elements as iron, vanadium, titanium, and zirconium that may be present in the yellow precipitate.

3. If appreciable amounts of titanium and zirconium are present, the phosphates of these elements will remain on the filter paper after treatment of the yellow precipitate with ammonium hydroxide, some running through to give a turbid filtrate. If the solution is not clear at this point, it must be refiltered after heating to boiling, the filter paper washed with hot water and ignited in a platinum crucible, the residue fused with a little sodium carbonate, the melt extracted with hot water, and the extract filtered and added to the ammoniacal solution of the ammonium phosphomolybdate. In this way the phosphorus in the insoluble phosphate is converted into sodium phosphate.

4. If arsenic is present, as it usually is in small amounts in steel, it is precipitated by the magnesia reagent and will be weighed with the magnesium pyrophosphate if it is not removed prior to the final precipitation. Boiling the magnesium ammonium phosphate solution in hydrochloric acid after addition of ammonium bromide reduces arsenate to arsenite and volatilizes arsenic as arsenious chloride.

5. Treatment of the ignited residue of magnesium pyrophosphate with acid followed by hydrofluorization of any insoluble matter serves to correct for any silica present in the weighed magnesium pyrophosphate.

6. It is to be noted that variations in the composition of the ammonium phosphomolybdate precipitate do not affect the result for phosphorus in this method.

2. ***Weighing phosphorus as*** $P_2O_5 \cdot 24\ MoO_3$. As stated above, ammonium phosphomolybdate can be dried at 110° to $(NH_4)_3PO_4 \cdot 12\ MoO_3$, or ignited to $P_2O_5 \cdot 24\ MoO_3$ at 450°; the latter weighing form is the better. It is convenient to use this method in place of the alkalimetric (see below) when only a few determinations are occasionally made. The small factor in this method is of distinct advantage. Concerning the accuracy of this method, see page 396.

Procedure. Precipitate ammonium phosphomolybdate as described in the magnesia method,[1] and collect the precipitate in a weighed porcelain filter crucible or a Gooch crucible that has been heated to 400°–450°. Wash the precipitate thoroughly with 5 per cent ammonium nitrate solution. Heat the precipitate in an electric furnace at 400°–450° for one hour. Repeat the heating to constant weight. If a furnace is not available, place the filter crucible inside a porcelain crucible and heat the latter to low redness over a burner. The residue should finally have a bluish-black color, with no admixture of yellow (undecomposed ammonium phosphomolybdate) or white (indicating too high a temperature of ignition). The residue is hygroscopic.

3. ***Alkalimetric method.*** In this method the ammonium phosphomolybdate is dissolved in a known amount of standard sodium hydroxide solution, and the excess of the latter is back-titrated with standard acid, phenolphthalein being used as indicator. From the amount of sodium hydroxide solution required to react with the precipitate, it is a simple matter to calculate the amount of phosphorus from the equation

$$(NH_4)_3PO_4 \cdot 12\ MoO_3 + 23\ NaOH \rightarrow 11\ Na_2MoO_4 + (NH_4)_2MoO_4 + NaNH_4HPO_4 + 11\ H_2O.$$

It will be seen that the calculation is based upon a precipitate of ideal composition, i.e., one in which the ratio of phosphorus to molybdic oxide is 1 to 12 and which contains no nitric acid.

Procedure.

Standard solutions: *0.1 N sodium hydroxide.* Dilute concentrated carbonate-free sodium hydroxide with equilibrium water to give an approximately 0.1 *N* solution (p. 552). Standardize against potassium biphthalate, using phenolphthalein as indicator (p. 554).

0.1 N nitric acid. Dilute 7 ml. of concentrated nitric acid to 1 liter. Standardize the solution by running a ratio against the standard sodium hydroxide solution, using phenolphthalein as indicator.

Weigh into a 250 ml. Erlenmeyer flask a 1 to 3 g. sample of steel, depending upon the phosphorus content, dissolve in nitric acid, and treat with potassium permanganate and sulfite as described under the magnesia method. After expulsion of sulfur dioxide, cool the solution to 30°, add 35 ml. of 6 *N* ammonium hydroxide[1] and 40 ml. of molybdate reagent. Stopper the flask, and shake the contents for five to ten minutes. Allow the precipitate to settle, and decant the supernatant liquid through a S. and S. No. 589 Blue Band filter paper. Wash the flask, precipitate, and paper twice with 5 ml. portions of 1 : 100 nitric acid and then thoroughly with a 1 per cent solution of potassium nitrate until the washings give no acid reaction with methyl orange. Place the paper in the original flask, add approximately 20 ml. of 0.1 *N* sodium hydroxide, and shake to dissolve the precipitate. If the precipitate does not entirely dissolve, add more sodium hydroxide solution and shake again until all is in solution. Then add 50 ml. of equilibrium water and 5 drops of 0.1 per cent phenolphthalein solution, and titrate with 0.1 *N* nitric acid, adding a few drops in excess. Finish the titration by adding sodium hydroxide to the first faint pink color.

---

[1] Any insoluble material in the solution must be filtered off before the molybdate reagent is added.

A blank should be run if the stoichiometric titer of the sodium hydroxide is to be used. The phosphorus titer of the sodium hydroxide solution can also be found empirically by standardizing against a steel (similar to the sample) of known phosphorus content.

NOTES:

1. The above directions apply to plain carbon steels and some alloy steels. Alloy steels mentioned in Note 1, under magnesia method, require slightly different treatment.

2. It is highly important that the ammonium phosphomolybdate precipitate obtained in the alkalimetric procedure have the proper ratio of phosphorus to molybdic oxide. For this reason, particular attention must be paid to the temperature of precipitation; if the temperature is too high, the precipitate will be enriched in molybdic oxide, and high results will be obtained for phosphorus. It is best to keep the temperature below 45° during the precipitation. Moreover, at higher temperatures the contamination of the precipitate by vanadium and arsenic is greater.

In the presence of the interfering elements mentioned in method 1, a longer period of precipitation must be used and more molybdate added.

3. The end point in the titration with phenolphthalein as indicator is not very sharp. At a pH of about 8 the molybdate is all present in the form of Na_2MoO_4; upon further addition of acid the pH decreases slowly with the formation of complex acid molybdates. For this reason phenolphthalein must be used as indicator. At the end point most of the phosphate is present in the form of Na_2HPO_4. The presence of the ammonium ion causes the end point to be vague. In order to neutralize all of the ammonia to ammonium ion, methyl red should be used as indicator; however, under these conditions a great portion of the molybdate would be transformed into the acid complexes. Since the amount of ammonia is small compared with the concentration of molybdate (see equation), only a small error is introduced by using phenolphthalein as indicator.

4. This method is a favorite routine procedure and is used when fairly accurate results must be obtained in a short period of time.

---

[1] A permanent precipitate of hydrous ferric oxide must not form.

Sulfur.

Two methods for sulfur will be described.[1] The first, involving the weighing of barium sulfate, is the more accurate.

1. *Gravimetric method: weighing of barium sulfate.*

Method. The steel is dissolved in concentrated nitric acid; and the sulfur, which exists in ferrous materials as sulfide, is thereby oxidized to sulfate:

$$3\,FeS + 12\,HNO_3 \rightarrow Fe(NO_3)_3 + Fe_2(SO_4)_3 + 9\,NO + 6\,H_2O.$$

Since nitrates and ferric iron are carried down to a large extent by barium sulfate (p. 331), it is necessary to remove or destroy these ions. Nitrate is removed by evaporating the solution with hydrochloric acid, and the dehydrated silica which separates at this point is later filtered off. Ferric iron is reduced to the ferrous state by treatment with zinc in acid solution, and the excess of the latter and silica are filtered off. In the filtrate, sulfate is precipitated by adding barium chloride; the barium sulfate is filtered off, washed, ignited, and finally weighed.

Procedure. Dissolve 5 g. of the sample in 50 ml. of concentrated nitric acid in a covered 250 ml. Erlenmeyer flask. If solution is slow, 5 ml. of hydrochloric acid may be added, a few drops at a time. When the sample has dissolved, add 0.5 g. of analytical-grade sodium chloride, evaporate to dryness, and bake on the hot plate for ten or fifteen minutes. Cool, add 30 ml. of concentrated hydrochloric acid, evaporate to dryness, and bake as before. Again add 30 ml. of hydrochloric acid, and evaporate the solution to a syrupy consistency. Now add 5 ml. of hydrochloric acid, 25 ml. of water, and 5 g. of 20–30-mesh sulfur-free zinc. Place the flask upon the steam bath, warm until all the ferric iron has been reduced and there is hardly any evolution of hydrogen. Filter the solution through a small filter, catching the filtrate in a 250 ml. beaker. Wash with 50 to 75 ml. of approximately 1 : 50 hydrochloric acid. Warm the solution to 70°, and precipitate the sulfate by adding 10 ml. of 10 per cent barium chloride solution. Allow the solution to stand at least eighteen hours. Filter off the precipitate on a dense filter (for example, S. and S. No. 589 Blue Band) and wash first with a solution containing 10 ml. of hydrochloric acid and 10 ml. of 10 per cent barium chloride in 1 liter of water to remove iron, and then with cold water to remove chlorides (test with silver nitrate). Not more than 50 to 75 ml. of water should be used for the last washing. Examine the filtrate and washings carefully for barium sulfate that might have run through the paper. Ignite the precipitate to constant weight in a weighed crucible over a Tirrill burner. For the best results use a platinum crucible, and treat the ignited residue with 1 drop of 12 N sulfuric acid and 0.5 to 1 ml. of hydrofluoric acid, evaporate to dryness, ignite again, and then weigh.

It is very important to run a blank determination, carrying it through all the steps of the determination itself. Report the percentage of sulfur found after applying the correction obtained in the blank.

---

[1] Sulfur may also be determined by burning the steel sample in a stream of oxygen, absorbing the sulfur oxides in dilute neutral hydrogen peroxide solution, and titrating the sulfuric acid formed with standard base. See, for example, C. H. Hale, Jr., and W. F. Muehlberg, Ind. Eng. Chem., Anal. Ed. 8. 317 (1936).

NOTES:

1. The above procedure can be used for most alloy steels as well as for cast iron; tungsten steels require special treatment.

2. Ferrous iron and zinc chloride are not carried down to any serious extent by barium sulfate. The precipitate of barium sulfate obtained in this procedure is never entirely pure, containing, for example, chloride and other substances as well, in the usual case. Certain constituents of alloy steels may contaminate the precipitate (chromium, tungsten, etc.); and when these are present, special steps must be taken to prevent their interference. Contamination of the precipitate by common contaminants (chloride) is not serious in this case on account of the relatively small amounts of sulfur present.

3. The precipitate must first be washed with a dilute solution of hydrochloric acid to prevent the hydrolysis of the heavy-metal salts present. Since barium sulfate is appreciably soluble in dilute acid solutions, even when barium chloride is present, as it is in the first wash solution, only the smallest volume required should be used. In very accurate work the barium sulfate dissolved by the wash solutions is recovered by evaporating the latter to dryness, taking up the residue in a small volume of water containing a little barium chloride and hydrochloric acid, filtering, washing, and igniting. According to Lundell, Hoffman, and Bright, the barium sulfate thus recovered is equivalent to 0.003 per cent or less of sulfur on 4.57 g. (factor weight) of sample.

4. The use of gas for heating should be avoided in the procedure (except in the ignition of the barium sulfate) to prevent the introduction of sulfur.

2. *Evolution method.*

Method. This method involves the evolution of hydrogen sulfide by solution of the sample in hydrochloric acid, the absorption of the hydrogen sulfide in an ammoniacal solution of zinc sulfate or cadmium chloride with the formation of zinc or cadmium sulfide, and the titration of the sulfide in an acid solution with a standard solution of iodine. A solution of potassium iodate containing an excess of potassium iodide is advantageously used as the standard iodine solution; in acid solution iodate and iodide react to give iodine, which oxidizes the sulfide to sulfur:

$$IO_3^- + 5\,I^- + 6\,H^+ \rightarrow 3\,I_2 + 3\,H_2O$$
$$H_2S + I_2 \rightarrow S + 2\,I^- + 2\,H^+.$$

Starch is used to indicate the end point.

It will be seen that this method of determining sulfur is based upon the assumption that the sulfur exists in the sample entirely in the form of sulfide and that all the sulfur is evolved as hydrogen sulfide on treatment with acid. Since these conditions are not entirely met, the method is not as accurate as the gravimetric method; but on account of its great rapidity it is very often used, especially in control laboratories where the nature of the sample is known. The accuracy of the method can be increased by standardizing the iodine solution against a steel of known sulfur content as much as possible like the sample analyzed in its characteristics.

Procedure.

Apparatus: A 250 ml. Florence flask with a two-hole rubber stopper carrying (1) a thistle tube extending nearly to the bottom of the flask and (2) a spray trap to which is connected a delivery tube dipping nearly to the bottom of a 250 ml. Erlenmeyer flask.

Solutions: *Ammoniacal zinc sulfate.* Dissolve 20 g. of zinc sulfate heptahydrate in 100 ml. of water, and add 100 ml. of concentrated ammonium hydroxide. Filter off any precipitate formed on standing.

Potassium iodate-potassium iodide. Dissolve approximately 1.1 g. of pure dry potassium iodate, weighed to the nearest milligram, and 12 g. of potassium iodide in exactly 1 liter of water. Calculate the sulfur titer of the solution from the amount of potassium iodate weighed out.

Starch, 0.2 per cent (see p. 619). The solution must give a sharp color change with iodine.

Place 5 g. of steel in the flask, replace the stopper, and dip the delivery tube into the Erlenmeyer containing 100 ml. of water and 10 ml. of ammoniacal zinc sulfate solution. Pour 80 ml. of 1 : 1 hydrochloric acid into the flask through the thistle tube, and heat with a flame so that there is a rapid steady evolution of gas. Boil for one minute after the sample has dissolved, and then disconnect the delivery tube, leaving it in the beaker for a stirrer. Cool the solution to room temperature if necessary, add 5 ml. of 0.2 per cent starch solution and 40 ml. of 1 : 1 hydrochloric acid, and titrate immediately with the potassium iodate-iodide solution to the first permanent blue color.

NOTES:

1. Since the method is more or less empirical, the directions must be followed exactly. Thus, it is not permissible to take a sample that weighs much more or less than 5 g., for then the percentage of sulfur found will be appreciably different.

2. The following table contains some results for the determination of sulfur in Bureau of Standards irons and steels by the oxidation and the evolution method as given in the Bureau's certificates:

MATERIAL	PERCENTAGE OF SULFUR	
	Weighing as $BaSO_4$	Evolution as H_2S
Cast iron No. 4d	0.075	0.072
Bessemer steel No. 8d	0.083	0.084
B.O.H. steel No. 11d	0.041	0.041
Cr-V steel No. 30c	0.014	0.013
Ni steel No. 33b	0.032	0.031

Most cast irons and some alloy steels give erroneous results.

Silicon.

Method. The steel or iron is dissolved in sulfuric, perchloric, or hydrochloric acid (sometimes with the aid of an oxidizing agent such as nitric acid), and the solution is evaporated to fumes in case sulfuric acid or perchloric acid was employed to effect solution, or to dryness if hydrochloric acid was used, in order to dehydrate the silica and thus render it insoluble. Water or acid is then added to dissolve soluble salts, and the silica is filtered off. Single dehydrations never yield all the silica; a second dehydration recovers nearly all of the remainder. However, in all but the most accurate work a single evaporation will suffice, provided that the percentage of silicon in the material is not greater than 0.5 per cent. The silica thus obtained is not pure. It is ignited at a high temperature and weighed as anhydrous silica plus contaminants, then treated with hydrofluoric acid in the usual way to volatilize silica, and the residue weighed. The loss in weight gives the amount of silica (p. 404).

Procedure (*sulfuric acid method*). Transfer a 5 g. sample to a 300 ml. casserole and dissolve in 125 ml. of 1 : 5 sulfuric acid. Solution is aided by gentle warming. (The determination may be made more rapidly by using dilute hydrochloric acid to dissolve the sample and then adding sulfuric acid.) Evaporate the solution to fumes of sulfuric acid, taking precautions against spattering. When dense fumes have been given off for about three minutes, remove the casserole from the heat and allow to cool somewhat. Then add all at once 100 ml. of water warmed to 40°. Stir the liquid to bring salts into solution, heating somewhat if necessary but not to boiling. Without delay filter off the silica on a rapid paper (S. and S. No. 589 Black Band). With a policeman dislodge the silica adhering to the walls of the casserole. Wash the precipitate with 1 : 20 hydrochloric acid until the iron salts have been washed out (about six times will suffice), and then a few times with hot water. Place the paper and precipitate in a platinum crucible, heat slowly to char the paper and burn off the carbon, and then apply the full flame of a Meker burner. If an electric muffle is used, regulate the temperature to 1050°–1150°. When constant weight has been attained, add a few drops of 1 : 1 sulfuric acid to the residue and then approximately 5 ml. of hydrofluoric acid. Evaporate the hydrofluoric acid, and fume off the sulfuric acid in a radiator. Ignite the residue strongly and weigh again. In very accurate work a blank should be run.

Report the percentage of silicon.

NOTES:

1. A 5 g. sample is suitable for steels containing less than 0.5 per cent of silicon; for higher silicon contents a smaller sample should be taken. For cast iron a 1 g. sample should be used. Alloy steels can be analyzed by the above procedure if they dissolve in sulfuric or hydrochloric acid, else nitric acid with or without hydrochloric acid must be used (see Tungsten).

2. Silicon exists as iron silicide in steels and in cast iron. There is no danger of losing silicon as the hydride by dissolving the sample in a nonoxidizing acid.

3. The following table indicates the results obtained for silicon in steels by dehydration with various acids.[1]

---

[1] R. M. Fowler, Ind. Eng. Chem., Anal. Ed. *4*, 382 (1932).

Silicon Obtained in Single Evaporations

Steel	Percentage of Silicon Present	Percentage of Silicon by Several Methods			
		H_2SO_4	HNO_3	$HClO_4$	HCl
Silicon steel	4.70	4.66	4.60	4.67	4.63
Acid electric steel	0.450	0.435	0.431	0.436	0.428
A.O.H. steel	0.112	0.105	0.105	0.106	0.103

The chief advantage in the use of perchloric acid lies in the easy solubility of the anhydrous perchlorates. Perchloric acid is profitably used for dehydration when appreciable amounts of chromium or nickel are present in the sample; these metals yield difficultly soluble sulfates when sulfuric acid is used for dehydration.

4. The ignited silica always contains greater or lesser amounts of foreign substances, depending upon the constituents of the steel and the method used. Among the possible contaminants the following may be mentioned: aluminum oxide, titanium oxide, titanium phosphate, iron oxide, etc. The weight of the silica must be obtained by hydrofluorizing by the usual procedure. In the presence of phosphorus the sulfuric acid must be expelled at as low a temperature as possible after evaporation of the hydrofluoric acid to avoid loss of phosphorus. When tungsten is present in the hydrofluorized residue, the final ignition must be made below 800° to prevent volatilization of tungstic oxide.

Nickel.

Precipitation with dimethylglyoxime. This is the method most often used for the accurate determination of nickel.[1]

Method. An acid solution containing iron in the ferric state is treated with tartaric acid and an alcoholic solution of dimethylglyoxime. The addition of a slight excess of ammonia precipitates nickel quantitatively as nickel dimethylglyoxime, which is washed and weighed as such after drying at 100°–120° (p. 77).

The precipitate is insoluble in dilute ammonia, in acetic acid-acetate solutions, and in excess of reagent; it is soluble in strongly acid solutions and in solutions containing much alcohol. The presence of tartrate is required to prevent the precipitation of ferric iron in ammoniacal solutions; ferric iron forms a complex with tartrate from which iron cannot be precipitated as hydroxide by bases.

Large amounts of copper and cobalt retard the precipitation of nickel dimethylglyoxime, but the difficulty can usually be overcome by adding a sufficiently large excess of dimethylglyoxime and allowing more time for precipitation.

Unnecessarily large amounts of the reagent should be avoided, because dimethylglyoxime is not very soluble in water (or dilute alcohol) and may separate; if very much reagent is added, the solubility of the precipitate may become perceptible as a consequence of the alcohol introduced.

---

[1] O. Brunck, Z. angew. Chem. *20*, 834, 1844 (1907); *27*, 315 (1914).

The following directions apply to simple nickel steels.

Procedure. Weigh out a 1 g. sample into a 400 ml. beaker and dissolve in 50 ml. of 1 : 1 hydrochloric acid. Heat, if necessary, to hasten solution. Cautiously add 10 ml. of 1 : 1 nitric acid and boil for a few minutes to expel oxides of nitrogen. Dilute to 200 ml. and add 7 g. of tartaric acid. When the tartaric acid has dissolved, neutralize with concentrated ammonia and add approximately 1 ml. in excess. If any insoluble material is visible in the solution, filter it off on paper, and wash the latter with hot water. Make the solution slightly acid with hydrochloric acid, heat to about 80°, and add 20 ml. of a 1 per cent alcoholic solution of dimethylglyoxime. Add ammonia until the liquid is slightly ammoniacal, and set the solution aside for thirty to sixty minutes. Filter through a weighed filter crucible, and wash the precipitate with hot water until the washings give no reaction for chloride when tested with nitric acid and silver nitrate. Test the filtrate for complete precipitation by adding a little dimethylglyoxime solution. Dry the precipitate by heating in an oven at 100° to 120° for one hour. Repeat the heating to constant weight. The dried precipitate contains 20.32 per cent of nickel. Report the percentage of nickel in the steel.

NOTES:

1. The weight of sample specified is suitable for steels containing approximately 1 per cent of nickel. For lower or higher percentages, correspondingly larger or smaller samples should be taken.

2. When very small amounts of nickel are present, the solution should stand overnight before filtration.

Other methods. Nickel can be determined by electrolytic deposition. Cobalt and copper are deposited with the nickel; a number of substances which may be present in steel interfere. Nickel can also be determined volumetrically by titration with potassium cyanide (p. 574).

Chromium.

Nearly all methods for the determination of chromium in steel are based upon the oxidation of the element to chromate and the subsequent determination of the latter by volumetric methods (or colorimetrically if the amount is small). Volumetrically, chromate is determined by adding a measured amount of a reducing agent, usually ferrous sulfate, and back-titrating the excess of the reducing solution with permanganate, or by direct potentiometric titration with ferrous sulfate; in either case chromate is reduced to chromic salt.

Chromic salts can be oxidized to chromate in hot acid solution (the medium in which the oxidation is usually effected) by a number of oxidizing agents, of which the following may be mentioned: alkali persulfates in the presence of silver nitrate, perchloric acid, potassium permanganate, and potassium bromate. The excess of persulfate can be destroyed by boiling, and the excess of perchloric acid is rendered nonoxidizing by simple dilution with water. Vanadium, if present, is oxidized to vanadate,

$VO_4^{\equiv}$. Vanadate is reduced to the vanadyl state, VO^{++}, by ferrous sulfate, but the vanadyl ion is slowly reoxidized to vanadate by potassium permanganate in the back-titration, so that this element does not interfere seriously in the procedure if the titration is properly made. The end point, however, is not very satisfactory. Substitution of standard arsenite solution for ferrous sulfate is advantageous.

Since vanadium is so often found with chromium in steels, it is convenient to combine the determination of these two elements.

Vanadium.

The volumetric determination of vanadium involves either (a) the reduction of vanadate to the vanadyl stage, or (b) the oxidation of vanadyl salt to vanadate, with proper provision for the effect of interfering elements that may be present. Since the determination of vanadium is most often required in chrome-vanadium steels, we shall give procedures by which both of these elements can be determined at the same time.

Many methods have been proposed for the simultaneous determination of chromium and vanadium in steel. Directions for two different procedures are given here. These procedures are designed for the analysis of chrome-vanadium steels.

1. *Method of Willard and Young.*[1] In this method chromium and vanadium are oxidized to chromate and vanadate, respectively, with perchloric acid; and after diluting to destroy the oxidizing properties of perchloric acid, a measured excess of ferrous sulfate is added to reduce chromic and vanadic acids. The excess of ferrous sulfate is then determined by titration with standard potassium permanganate solution, *o*-phenanthroline-ferrous complex being used as oxidation-reduction indicator (p. 494). The reaction between vanadyl ions and permanganate in the solution of high acidity in which the titration is made is so slow that a good end point is obtained. After the titration of the excess ferrous sulfate, the acidity of the solution is reduced, and vanadyl ion is titrated with permanganate at 50°; at this temperature the reaction between the vanadyl salt and permanganate is rapid, and a second sharp end point is obtained with *o*-phenanthroline as indicator (vanadic acid does not possess a sufficiently high oxidation potential to affect the color of the indicator).

Procedure.

Solutions: *Potassium permanganate, 0.05 N.* Prepare and standardize in the usual manner.

Ferrous ammonium sulfate, 0.1 N, containing 20 ml. of sulfuric acid per liter. Standardize immediately before use by titrating with standard potassium permanganate in dilute perchloric acid solution, using *o*-phenanthroline-ferrous complex as indicator, as in the determination itself.

o-Phenanthroline-ferrous complex, 0.025 M solution.

Weigh a sample of suitable size (2 g. for low-chromium steels) into a 500 or 600 ml. beaker. Add 20 to 25 ml. of 70 per cent perchloric acid and warm gently, removing from the heat if the action becomes violent. After solution has been effected, boil the solution for fifteen or twenty minutes. Cool the beaker in the air for a moment and then place in cold water. Add 25 ml. of water (rinse off the cover glass) and boil the solution for three minutes. Dilute the liquid to 250 or 300 ml. and cool to room temperature. Add 20 ml. of 6 *M* phosphoric acid, and run in a measured excess of ferrous ammonium sulfate solution from a buret. After adding 3 drops of *o*-phenanthroline-ferrous iron complex, titrate with potassium permanganate solution until the color changes from pink to a clear green.

---

[1] H. H. Willard and Philena Young, Ind Eng. Chem., Anal. Ed. *6*, 48 (1934)

Now add sufficient crystallized sodium acetate to react with the perchloric acid present in the solution. The amount of sodium acetate required for this purpose may be estimated by assuming that 5.4 ml. of 70 per cent perchloric acid are required to dissolve and oxidize each gram of steel and that 1.6 g. of the salt will be needed for each ml. of acid remaining. Sodium acetate may also be added in small portions while the solution is being warmed until further addition would cause a permanent precipitate of ferric phosphate to form. Heat the solution to 50° (use a thermometer) and titrate slowly with potassium permanganate. The color change at the end point is from pink to green. There should be no return of the pink color within one minute. Report the percentages of chromium and vanadium.

2. *Method of Kolthoff and Sandell.*[1] This procedure involves the oxidation of chromium and vanadium in acid solution with potassium bromate,[2] and the destruction of the excess of the latter together with oxidized manganese by boiling with ammonium sulfate in the presence of a low concentration of hydrochloric acid. After cooling, a measured excess of standard arsenious acid is added; chromic acid is thereby reduced to chromic salt, whereas vanadate is unaffected (see Note 1). The excess of arsenious acid is titrated with permanganate in the presence of a trace of iodide as catalyst (Note 2), and the chromium thus determined. Vanadium is then determined in the same solution by titration with ferrous ammonium sulfate, diphenylbenzidine being used as indicator ($VO_4^{\equiv} \rightarrow VO^{++}$).

Procedure.

Solutions: *Arsenious acid, 0.1000 N*. Weigh out 4.947 g. of pure arsenious oxide, dissolve in 50 ml. of 1 *N* sodium hydroxide, dilute nearly to 1 liter, make neutral or slightly acid with hydrochloric acid, and then dilute to exactly 1 liter. If pure arsenious oxide is not available, make up an approximately 0.1 *N* solution, and standardize against standard permanganate solution.

Potassium permanganate, 0.025 N. Standardize against the arsenious acid solution (make the latter solution 1 *N* in hydrochloric acid, add 1 drop of 0.002 *N* potassium iodide solution, and titrate with permanganate to the first pink tinge), or standardize against sodium oxalate.

Ferrous ammonium sulfate, 0.025 N, in approximately 0.5 *N* sulfuric acid.

Potassium iodide solution (*catalyst*), *0.002 N*.

Diphenylbenzidine solution (*indicator*), 0.1 per cent in concentrated sulfuric acid.

---

[1] I. M. Kolthoff and E. B. Sandell, Ind. Eng. Chem., Anal. Ed. *2*, 140 (1930).

[2] Other oxidizing agents such as perchloric acid and potassium persulfate may, of course, be used instead of potassium bromate.

Weigh out a 2 to 3 g. sample (chromium content 1 per cent) into a 250 ml. Erlenmeyer flask, add 25 ml. of water, 1.5 ml. of concentrated sulfuric acid for each gram of steel, allowing a 1 to 2 ml. excess, and 3 to 4 ml. of 85 per cent phosphoric acid. Heat the liquid to hasten solution. When the sample has dissolved, add dropwise 1 ml. of concentrated nitric acid for each gram of steel. Boil to expel the oxides of nitrogen, and dilute the solution to 100 ml. Now add 1.5 g. of pure potassium bromate and boil for five minutes. Then add cautiously 5 g. of ammonium sulfate, and boil until most of the bromine has been expelled. Next add 10 ml. of 1 *N* hydrochloric acid, and boil until starch-iodide paper held at the mouth of the flask is no longer colored blue, indicating complete expulsion of bromine. The volume of the solution should be kept at 75 to 100 ml. during the boiling by the addition of water, if necessary.

Cool the solution to room temperature; add 6 to 8 ml. of 85 per cent phosphoric acid and 1 or 2 drops of 0.002 *N* potassium iodide. Run in standard arsenious acid solution from a buret until the color of the solution in the flask becomes green (indicating complete reduction of chromic acid); allow a few ml. of arsenious acid in excess. After three to five minutes back-titrate the arsenious acid with potassium permanganate; the end point is indicated by a sudden deepening in the color of the solution to bluish-green.

Add 1 drop of arsenious acid to reduce any permanganate present, and then sufficient sodium acetate to react with the acid present (allow approximately 5 g. of sodium acetate trihydrate for each ml. of concentrated sulfuric present, including also the acid in the indicator to be added, and 1.5 g. for each ml. of 12 *N* hydrochloric acid); no permanent precipitate should form. After the addition of 0.5 to 1.0 ml. of 0.1 per cent diphenylbenzidine indicator solution, allow the liquid to stand for approximately five minutes, and then titrate slowly with 0.025 *N* ferrous sulfate. The color change is from blue to green or bluish-green. Correct for the indicator blank by adding 0.03 ml. to the volume of the 0.025 *N* ferrous sulfate solution used for each 0.1 ml. of 0.1 per cent diphenylbenzidine solution added.

NOTES:

1. A slight reduction of vanadate by arsenious acid would lead to no error, because in the back-titration with potassium permanganate vanadyl ion would be reoxidized to vanadate ion.

2. Unless a trace of iodide (or iodate) is present as a catalyst in the titration of arsenite ion with permanganate, a quantitative reduction of the latter to manganous ion cannot be effected, a brown-colored solution containing trivalent or quadrivalent manganese being obtained. In the presence of a trace of potassium iodide and a low concentration of chloride, the reaction proceeds smoothly and rapidly, and an excellent end point is obtained.

3. In very accurate work the titration error should be experimentally determined, both for the chromic acid and the vanadic acid titration.

4. Regarding the use of oxidized diphenylamine sulfonic acid and diphenylamine as indicators in the vanadium titration, see Willard and Young, Ind. Eng. Chem., Anal. Ed. *5*, 154, 158 (1933); if the diphenylamine sulfonic acid is used as indicator, vanadium can be titrated in the presence of tungsten.

Molybdenum.

A rapid method for the determination of molybdenum in steels has been given by Knowles.[1] In this method the element is quantitatively precipitated in acid solution by the addition of α-benzoinoxime, and the precipitate is ignited to molybdic oxide (MoO_3). The only other elements that are precipitated by the reagent in mineral acid solution are tungsten, sexivalent chromium, quinquevalent vanadium, palladium, and tantalum. Chromium and vanadium do not interfere when they are reduced to the trivalent and quadrivalent state, respectively. Tungsten in the precipitate is corrected for as described in the procedure below.

Procedure.

Reagent: 2 per cent solution of *α-benzoinoxime* in 95 per cent alcohol.

Wash solution: 50 ml. of *reagent* and 10 ml. of *sulfuric acid* diluted to 1 liter.

Dissolve a 1 g. sample of steel in 50 ml. of 1: 5 sulfuric acid, and treat the hot solution with the minimum amount of nitric acid required to oxidize the molybdenum and decompose carbides (1 ml. will suffice for a 1 g. sample). Boil the solution to expel oxides of nitrogen, and filter if the liquid is not perfectly clear. Dilute to 100 ml., cool, and add enough ferrous ammonium sulfate solution to reduce vanadic and chromic acids. Cool the solution to 5° to 10°, add 10 ml. of α-benzoinoxime reagent, then bromine water to impart a distinct color to the liquid, and finally a few more ml. of reagent. Allow the mixture to stand for ten minutes, and then filter through a S. and S. No. 589 Black Band paper. Wash the precipitate with 150 ml. of cold fresh wash solution. Transfer the paper and precipitate to a weighed crucible, and char the paper at a low temperature. Then place the crucible in an electric muffle and ignite to constant weight at 500°–525°. Treat the residue with a few ml. of warm 1 : 3 ammonium hydroxide, and filter through a small filter if any insoluble material remains. Wash the filter thoroughly with warm water containing a little ammonium hydroxide, and reserve the filtrate and washings. Ignite the paper containing the insoluble residue, and weigh. Deduct this weight from the weight of the molybdic oxide. Examine the filtrate and washings for tungsten by adding excess hydrochloric acid and a little cinchonine solution (see Tungsten), and digest overnight. If a precipitate of tungsten is formed, filter it off, wash it, and ignite to the oxide at 525°. Deduct the weight of tungstic oxide from the weight of molybdic oxide. Report the percentage of molybdenum.

NOTES:

1. Molybdenum is precipitated in cold solutions in the presence of bromine to prevent possible reduction of the element to lower valence states by the α-benzoinoxime before complete precipitation.

From two to five times the theoretical amount of α-benzoinoxime should be used for the precipitation; 5 ml. of reagent suffice to precipitate 0.01 g. of molybdenum.

The solution should not be allowed to stand long before filtration. Low results are obtained if the precipitate stands one-half hour before the fitration is begun. Precipitation is complete within a few minutes after the addition of reagent.

---

[1] H. B. Knowles, Bur. Standards J. Research *9*, 1 (1932).

Molybdenum α-benzoinoxime cannot be dried at a low temperature and used as weighing form.

2. The temperature of ignition of molybdic oxide must be carefully controlled. The oxide begins to volatilize at 550°, but the rate of loss is very slow below 600°. The most suitable ignition temperature is 500°–525°.

3. The treatment of the ignited molybdic oxide with ammonium hydroxide serves to correct for the presence of substances such as ferric oxide and silica that have been carried down by the precipitate. These are insoluble in ammonia, whereas molybdic oxide (and tungstic oxide if present) is readily soluble, ammonium molybdate being formed.

4. If tungsten is present in the steel, it will be precipitated by the reagent and must be precipitated from the ammoniacal solution of the ignited residue by addition of hydrochloric acid and cinchonine, ignited to the oxide, and the weight of the residue deducted from that of the impure molybdic oxide.

5. The following results obtained by Knowles (*loc. cit.*) in the analysis of Bureau of Standards steels for molybdenum indicate the accuracy of the method:

Steel	Percentage of Molybdenum	
	Added or Present	Found
Chrome-molybdenum steel No. 72	0.149	0.166 0.160
B.O.H. steel No. 11d	0.51	0.52
	5.13	5.15

Tungsten.

Method. The steel is treated with hydrochloric or sulfuric acid, and the tungsten oxidized to tungstic acid, H_2WO_4, by the addition of nitric acid. Tungstic acid, being sparingly soluble in acid solutions, separates nearly completely on digestion. By adding the alkaloid cinchonine, the precipitation of tungsten can be made quantitative, the last small amounts of the element being precipitated as cinchonine tungstate. The tungstic acid thus separated is never pure but contains greater or less amounts of silica, iron oxide, and such elements as chromium, vanadium, and molybdenum, if these are present in the steel. The precipitate of tungstic acid is filtered off, washed, ignited at a low temperature, and treated with hydrofluoric acid and sulfuric acid to volatilize silica as silicon tetrafluoride:

$$SiO_2 + 4\ HF \rightarrow SiF_4 + 2\ H_2O.$$

Tungsten is not volatilized. The residue is ignited at not too high a temperature and weighed. The ignited residue is impure tungstic oxide containing such contaminants as mentioned above. To obtain the weight of tungstic oxide, it is necessary to determine the weight of the impurities and deduct the latter from the weight of the crude oxide. For this purpose the residue is fused with sodium carbonate; tungstic oxide is thus converted into water-soluble sodium tungstate, whereas iron remains as insoluble ferric oxide, which can be filtered off, weighed, and its weight deducted from that of the impure tungstic oxide. If elements such as chromium, vanadium, and molybdenum are present in the impure oxide, they are converted into soluble sodium chromate, vanadate, and molybdate, respectively, and must be determined in the filtrate by colorimetric methods.

Procedure. Weigh a 2 g. sample into a 400 ml. beaker, add 50 ml. of 1 : 1 hydrochloric acid, and heat. When the decomposition is complete, remove the vessel from the heat and add carefully 10 ml. of 1 : 1 nitric acid. Digest the mixture at 90°–100° until the separated tungstic acid is bright yellow; no dark particles should be visible in the mixture. Dilute the liquid to 100 ml., add 5 ml. of cinchonine solution (10 per cent solution in 1 : 1 hydrochloric acid), and digest slightly below the boiling point for thirty to forty-five minutes. Filter off the precipitate on a retentive quantitative filter paper and wash thoroughly with cinchonine wash solution (25 ml. of the cinchonine reagent solution diluted to 1 liter). Fold up the filter paper and place it in a weighed platinum crucible. Dry the paper and its contents by heating over a low flame, char the paper, and burn off the carbon at the lowest possible temperature. Cool the crucible, and add 1 or 2 drops of 1 : 1 sulfuric acid and about 2 ml. of hydrofluoric acid. Evaporate off the hydrofluoric acid and expel the sulfuric acid (preferably in a radiator). Ignite the residue at 750°–850°, best in a muffle furnace. If no furnace is available, heat the covered crucible to low redness over a Tirrill burner. Cool and weigh to obtain the weight of $WO_3 + Fe_2O_3$, etc. Fuse the weighed residue with 5 g. of purest anhydrous sodium carbonate. Extract the cold melt with 75–100 ml. of water, and filter off any insoluble material on a quantitative filter paper; rinse out the crucible carefully, and wash the residue and paper thoroughly. Place the filter in the crucible, char the paper, burn off the carbon, and fuse the residue with 0.5–1 g. of sodium carbonate. Take up the cooled melt in 25 ml. of water, filter, and wash the crucible and paper with hot water. The second filtrate is to be combined with the first and reserved if chromium, vanadium, and molybdenum are to be determined (Note 1). Place the filter in the crucible and ignite to obtain the weight of ferric oxide. Deduct the weight of ferric oxide from the weight of impure tungstic oxide to obtain the weight of tungstic oxide. Calculate the percentage of tungsten.

NOTES:

1. If the steel contains chromium, vanadium, and molybdenum in appreciable amounts, these elements should be determined colorimetrically in the combined filtrates from the sodium carbonate fusion, and the ignited residue of tungstic oxide corrected for the amounts found. For the details of this procedure the student is referred to Lundell, Hoffman, and Bright, *The Chemical Analysis of Iron and Steel*, page 330.

2. In accurate work a blank must be run on the sodium carbonate to correct for the insoluble impurities it may contain.

Simultaneous determination of silicon and tungsten.

It is sometimes convenient to determine both silicon and tungsten in the same sample. This can be done by precipitating tungstic acid and silica, and obtaining the weight of the combined ignited residue of SiO_2 and WO_3, treating with hydrofluoric and sulfuric acids to volatilize silica, and reweighing. The loss in weight gives the amount of SiO_2 present in the mixture, and the weight of the hydrofluorized residue gives the amount of WO_3 (Fe_2O_3, etc.).

Procedure. Take a 2 g. sample of steel and precipitate tungstic acid, as described above, with cinchonine. Filter off the tungstic acid, wash it, and reserve the precipitate. Evaporate the filtrate and combined washings to dryness, and heat the residue for an hour at 105°–110°. Add 10 ml. of concentrated hydrochloric acid to the residue, warm for a few minutes, dilute to 100 ml. with water, and warm until all salts have dissolved. Filter off the silica, and wash it with 1 : 20 hydrochloric acid and finally one or two times with approximately 1 : 50 sulfuric acid.

Silicon. Place the filter papers containing tungstic acid and silica in a weighed platinum crucible, dry and char the papers, and burn off the carbon at a low temperature. Ignite at 750°–850° in an electric furnace or, less preferably, over a Tirrill burner. After weighing the crucible and its contents, add one or two drops of 1 : 1 sulfuric acid and 3 ml. of hydrofluoric acid. Evaporate the hydrofluoric acid without boiling the liquid, and fume off the sulfuric acid. Ignite the residue at 750°–850°. The loss in weight represents the amount of silica. Report the percentage of silicon.

Tungsten. The residue of impure tungstic oxide left in the crucible is to be corrected for ferric oxide as described above under tungsten. Calculate the percentage of tungsten.

NOTE:

If silica is to be determined very accurately in a tungsten steel, its determination should not be combined with that of tungsten. A temperature of 1000°–1100°, or even higher, is needed to remove the last traces of water from silica, and at these temperatures tungstic oxide volatilizes.

BOOKS ON ANALYSIS OF FERROUS MATERIALS

O. Bauer and E. Deiss, *Sampling and Analysis of Irons and Steels*, translated by W. T. Hall and R. S. Williams, McGraw-Hill Book Co., New York, 1915.

A. A. Blair, *The Chemical Analysis of Iron*, 8th ed., J. B. Lippincott, Philadelphia, 1918.

Chemists' Committee of the Subsidiaries of the U. S. Steel Corporation, *Sampling and Analysis of Carbon and Alloy Steels*, Reinhold Publishing Corporation, New York, 1938.

W. T. Hall and R. S. Williams, *Chemical and Metallographic Examination of Iron, Steel, and Brass*, McGraw-Hill Book Co., New York, 1921.

F. Ibbotson, *The Chemical Analysis of Steel-Work's Materials*, Longmans, Green and Co., London, 1920.

C. M. Johnson, *Rapid Methods for the Chemical Analysis of Special Steels*. 4th ed., John Wiley and Sons, New York, 1932.

J. Kassler, *Untersuchungsmethoden für Roheisen, Stahl und Ferro-Legierungen*, F. Enke, Stuttgart, 1932.

A. Ledebur, *Leitfaden für Eisenhüttenlaboratorien*, 12th ed. by H. Kinder and A. Stadeler, 1925.

N. W. Lord and D. J. Demorest, *Metallurgical Analysis*, 5th ed., McGraw-Hill Book Co., New York, 1924.

G. E. F. Lundell, J. I. Hoffman, and H. A. Bright, *Chemical Analysis of Iron and Steel*, John Wiley and Sons, New York, 1931.

F. C. Phillips, *Methods for the Chemical Analysis of Ores, Iron, and Steel*, Chemical Publishing Co., New York, 1920.

H. F. Scobie, *Chemical Analysis for the Foundry Control Laboratory*, Swift and Co., St. Louis, 1942.

W. W. Scott, *Technical Methods of Metallurgical Analysis*, D. Van Nostrand Co., New York, 1923.

F. T. Sisco, *Technical Analysis of Steel and Steel Works Materials*, McGraw-Hill Book Co., New York, 1923.

U. S. Steel Corporation, *Methods of the Chemists of the U. S. Steel Corporation for the Sampling and Analysis of Alloy Steels*, 2nd ed., Carnegie Steel Co., Pittsburgh, 1921.

U. S. Steel Corporation, *Methods of the Chemists of the U. S. Steel Corporation for the Sampling and Analysis of Ferro-Alloys and Bearing Metals*, Carnegie Steel Co., Pittsburgh, 1921.

U. S. Steel Corporation, *Methods of the Chemists of the Subsidiary Companies of the U. S. Steel Corporation for the Sampling and Analysis of Pig Iron*, Carnegie Steel Co., Pittsburgh, 1934.

U. S. Steel Corporation, *Methods for the Commercial Sampling and Analysis of Iron Ores*, 2nd ed., Carnegie Steel Co., Pittsburgh, 1914.

United Steel Companies, *Standard Methods of Analysis of Iron, Steel, and Ferro-Alloys*, Sheffield, England, 1933.

R. Weihrich, *Die Chemische Analyse in der Stahlindustrie* (Vol. 31 in *Die Chemische Analyse*), F. Enke, Stuttgart, 1939.

PROBLEMS

1. Why is the presence of hydrochloric and hydrofluoric acids objectionable in the bismuthate method for manganese?

2. Devise a method for determining the amount of active oxygen in sodium bismuthate.

3. What volume of 4 N nitric acid will be required to dissolve 1 g. of iron if it be assumed that the acid is reduced to NO?

4. The permanganic acid formed in the oxidation of a 1.010 g. sample of steel by the bismuthate method was treated with 50.00 ml. of 0.0320 N ferrous ammonium sulfate solution. If 10.18 ml. of 0.0203 N potassium permanganate solution were required for the back-titration of the ferrous solution, what is the percentage of manganese in the sample?

5. The $(NH_4)_3PO \cdot 12\ MoO_3$ precipitate obtained from a 1.000 g. sample of steel was dissolved in 10.00 ml. of 0.1022 N sodium hydroxide solution, and the excess of base was back-titrated with standard nitric acid, phenolphthalein being used as indicator. If 6.05 ml. of 0.1010 N acid were required, what is the percentage of phosphorus in the sample?

6. What weight of sample must be taken in the determination of phosphorus in order that each milligram of ignited magnesium pyrophosphate shall represent 0.01 per cent of phosphorus?

7. A 5.00 sample of steel run for sulfur by the evolution method required 5.2 ml. of potassium iodate-iodide solution (1.000 g. KIO_3 and 10.00 g. KI in 1 liter) for the titration of the zinc sulfide in acid solution. Calculate the percentage of sulfur.

8. Why should iron be oxidized to the ferric condition before the precipitation of nickel with dimethylglyoxime?

9. Write equations for all the important reactions occurring in the determination of chromium and vanadium by either of the procedures given.

10. (a) In the determination of vanadium by titration with ferrous iron, what weight of sample must be taken in order that each milliliter of 0.020 *N* ferrous ammonium sulfate shall correspond to 0.100 per cent of vanadium?

(b) What volume of sodium arsenite solution containing the equivalent of 5.000 g. of As_2O_3 per liter is required to reduce the dichromate yielded by a 2.00 g. sample of steel containing 1.00 per cent of chromium?

CHAPTER XLV

ANALYSIS OF SILICATE ROCKS

The analysis of a silicate rock is one of the more difficult types of analysis, and one which serves to illustrate the general procedure followed in the analysis of complex inorganic materials wherein a large number of elements must be determined. The procedure adopted in the analysis of silicate rocks is applied with modifications in the analysis of such commercially important materials as glass, cement, and refractories, and is used as well in the mineral analysis of water. Silicate minerals are analyzed in much the same manner as silicate rocks, although not infrequently variations in procedure must be introduced to provide for elements that are not found in appreciable amounts in rocks or to allow for the greater proportion in which some elements occur in minerals.

The directions that follow are intended for the analysis of igneous silicate rocks, but the procedures can be applied with little or no modification to most metamorphic and sedimentary silicate rocks. For a detailed treatment of the subject of rock analysis, reference must be made to special works.[1]

Composition of silicate rocks.

Table LXXI, which gives the average composition of the igneous rocks of the world, serves to indicate the elements that are found in silicate rocks and their relative abundance. The oxides of silicon, aluminum, ferrous and ferric iron, magnesium, calcium, sodium, potassium, and hydrogen make up 98 per cent or more of the mass of igneous rocks. In addition to these very common constituents that are present in practically every specimen of igneous silicate rock, small amounts of titanium, phosphorus, and manganese are nearly universally present. The table shows that many other elements occur in very small amounts.

The percentages of the principal constituents of silicate rocks may vary over a wide range. Silica, the main constituent of these rocks, always occurs in large amounts, usually falling within the limits 40 to 80 per cent. The other oxides are more variable, and, depending upon the kind of rock,

[1] See especially:

W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*, pp. 645–818, John Wiley and Sons, New York, 1929. W. F. Hillebrand, *The Analysis of Silicate and Carbonate Rocks*, Bull. U. S. Geol. Survey No. 700, Government Printing Office, Washington, D. C., 1919. H. S. Washington, *The Chemical Analysis of Rocks*, 4th ed., John Wiley and Sons, New York, 1930. A. W. Groves, *Silicate Analysis*, T. Murby, London, 1937. W. van Tongeren, *Gravimetric Analysis*, D. B. Centen, Amsterdam, 1937.

The methods of analysis described in this chapter are mostly those used by Hillebrand and Washington.

they may range from practically zero up to the following maximum percentages: Al_2O_3, 30; CaO, 25; MgO, 50; FeO, 35; K_2O, 18. Certain of the minor constituents display a distinct tendency to occur in appreciable amounts in certain types of rocks only. Thus chromium occurs almost exclusively in ferromagnesian rocks; zirconium, in rocks rich in silica, especially those high in sodium; etc.

Constituents determined in rock analysis.

Of the constituents that occur in rocks, some are more important than others; and it is thus convenient to divide them into two classes, comprising respectively the major and minor constituents. Washington[1] makes the following division:

Major constituents: SiO_2, TiO_2, Al_2O_3, Fe_2O_3, FeO, MnO, MgO, CaO, Na_2O, K_2O, H_2O + (> 110°), H_2O − (< 110°), and P_2O_5.

Minor constituents: CO_2, ZrO_2,[2] $(Ce, Y)_2O_3$, Cr_2O_3, V_2O_3, NiO, CoO, BaO, SrO, BeO, CuO, F, Cl, SO_3, S, and B_2O_3.

TABLE LXXI. AVERAGE COMPOSITION OF IGNEOUS ROCKS[3]

CONSTITUENT	PERCENTAGE	CONSTITUENT	PERCENTAGE
SiO_2	59.14	F	0.030
Al_2O_3	15.34	S	0.052
Fe_2O_3	3.08	P_2O_5	0.299
FeO	3.80	Cr_2O_3	0.055
MgO	3.49	V_2O_3	0.026
CaO	5.08	MnO	0.124
Na_2O	3.84	NiO	0.025
K_2O	3.13	BaO	0.055
H_2O	1.15	SrO	0.022
TiO_2	1.05	Li_2O	0.008
ZrO_2	0.039	Cu	0.010
CO_2	0.101	Zn	0.004
Cl	0.048	Pb	0.002

In a satisfactorily complete rock analysis, all thirteen of the major constituents must be determined. In this chapter directions for the determination of all the major constituents and some of the minor ones are given

Preparation of the sample.

Depending upon the grain coarseness of the rock, from 25 to 100 g. of a representative field sample should be at hand. From this amount usually not less than 10 g. of 100-mesh powder should be prepared. This quantity will suffice for the determination of all the constituents considered here, and indeed there will be enough for a reanalysis if necessary. In the rather unusual case that many minor constituents are to be determined, a larger amount of finely powdered sample will have to be prepared.

---

[1] H. S. Washington, *The Chemical Analysis of Rocks*, p. 11.

[2] This constituent added to Washington's list by the authors.

[3] F. W. Clarke, *Data of Geochemistry*, Bull. U. S. Geol. Survey No. 770 (1924), p. 29.

Procedure. Break the rock into ½ to 1 cm. pieces by placing the large pieces on a hardened steel plate and striking with a hardened hammer. If such a plate is not available, break the rock on the top of the pestle of the Plattner mortar. Prevent as far as possible the loss of fragments. Then crush the whole sample to a coarse powder in the Plattner ("diamond") mortar (Fig. 40, p. 192) placed on a firm foundation. Place one or two small fragments in the mortar, put the pestle into position, and strike it lightly with a hammer until the pieces have been reduced to a rather coarse powder with no very large fragments. Avoid *grinding* the powder; hold the pestle vertically with a firm grasp in the hand, and do not let it rub against the walls of the mortar unnecessarily. Deliver strictly vertical blows with the hammer. After each portion has been crushed, pour the powder out on a large sheet of glazed paper, avoiding the raising of any dust. Continue in this manner until the whole sample (25 to 75 g. or more) has been reduced to a coarse powder and transferred to the paper. Now mix the powder thoroughly by raising the corners of the paper in succession and causing the powder to roll over itself. Flatten out the cone thus formed with a spatula, quarter, and transfer one half of the powder (opposite quarters) directly to a 100-mesh sieve if 25 g. or so of rock were pulverized; or quarter again if 50 to 75 g. were taken. Sieve [1] the powder gently onto a new piece of glazed paper, being careful to raise as little dust as possible; hold the sieve close to the paper. Transfer a small portion of the coarse powder remaining on the sieve to an agate mortar and grind therein,[2] return to the sieve, and continue in this manner until nearly all the powder has passed through. Grind the last small portion remaining on the sieve in the mortar, and transfer directly to the paper. All of the quartered sample must finally find its way to the paper. Mix the 100-mesh powder very carefully on the paper as described before, and transfer the powder to a stoppered vial.

DETERMINATION OF SILICA, ALUMINUM, TOTAL IRON, TITANIUM, CALCIUM, AND MAGNESIUM

Method.

These are all determined in one sample, "the main portion." The rock powder is decomposed by fusion with sodium carbonate, the cake is treated with hydrochloric acid, and the silica is dehydrated in the usual way and filtered off. The ignited silica is treated with hydrofluoric and sulfuric acids, and the amount of silica is obtained from the loss in weight (p. 404). To the silica thus found there must be added the small amount still remaining in solution, which is subsequently carried down by the ammonia precipitate and later recovered.

---

[1] A sieve with silk bolting cloth is best, but one of metal will do if the rock is not to be examined for the metals of which the sieve is composed.

[2] If the powder is too coarse to grind easily in the agate mortar, it may be necessary to pulverize it further in the steel mortar. Reserve the portion of the sample crushed in the Plattner mortar but not ground in agate for use in case the finely ground portion should become exhausted.

The filtrate from the silica is treated with ammonium hydroxide to precipitate iron, aluminum, titanium, zirconium, and phosphorus.[1] The precipitate of the hydrous oxides is dissolved in hydrochloric acid and again precipitated by ammonium hydroxide. A double precipitation is necessary to minimize the coprecipitation of magnesium, calcium, and sodium. The precipitate is ignited, and the weight of the mixed oxides, Al_2O_3, Fe_2O_3, TiO_2, ZrO_2, and P_2O_5, is obtained. The oxides are next converted into sulfates by fusion with alkali pyrosulfate, and the melt is dissolved in dilute sulfuric acid. The small amount of silica which escaped separation in the dehydration is recovered at this point.

Total iron is determined in the solution of the sulfates by reducing with hydrogen sulfide (or other reducing agent) and titrating the ferrous salt with potassium permanganate. Titanium can be determined in the solution remaining from the titration of the iron by adding hydrogen peroxide and comparing the intensity of the color of the yellow solution thus obtained with a peroxidized titanium solution of known strength. The direct determination of aluminum in the complex ammonia precipitate is so difficult that this element is found by difference after phosphorus (and possibly other constituents of the mixed oxide residue) has been determined in a separate portion as described later.

The combined filtrates from the ammonia precipitate will contain the calcium, magnesium, and manganese. Calcium is precipitated from this solution in the usual way with oxalate, a double precipitation being made. Magnesium is precipitated in the combined filtrates from the calcium oxalate with ammonium phosphate or 8-hydroxyquinoline. A correction must be applied for the manganese in the precipitate by determining it colorimetrically and deducting the amount found.

Decomposition of the sample.

Weigh out 1.0 g. of the finely powdered air-dry sample into a platinum crucible (30 ml. size) and decompose with purest sodium carbonate as described on page 406, using 5–6 g. of sodium carbonate for rocks high in silica, such as granites, and 8–9 g. for rocks low in silica.

Silica.

Proceed as directed on page 407 *et seq.* in determining silica. Make two evaporations to dehydrate the silica.[2] Treat the weighed ignited residue with hydrofluoric and sulfuric acids, and find the silica by difference. Reserve the crucible containing the hydrofluorized residue. To the value for silica thus obtained, there must be added the small amount later isolated from the hydrous oxide precipitate (p. 739).

---

[1] The presence of manganese gives rise to slight difficulties at this point. It would be desirable to precipitate this metal here, but this is not so easily done. The use of bromine water to oxidize the manganese is not to be recommended because the oxidation — and therefore the precipitation — of manganese is incomplete, especially since a reprecipitation is made. Ammonium persulfate appears to be somewhat better than bromine for the oxidation, but the introduction of the large amounts of sulfate resulting from its decomposition is not entirely unobjectionable. In the procedure here described, manganese is allowed to go into the filtrate. With the small amounts of manganese found in rocks, the ammonia precipitate will be found practically free of the element after reprecipitation if the operations are correctly performed. Most of the manganese will then come down with the magnesium ammonium phosphate later, and in accurate work it must be determined colorimetrically therein to obtain the true amount of magnesium.

[2] A platinum dish or basin is generally to be preferred for the evaporations, but

Precipitation and ignition of the hydrous oxides of aluminum, iron, titanium, together with phosphorus and possibly other elements.[1]

If the evaporation of the hydrochloric acid solution for the dehydration of silica was conducted in platinum, add a few drops of saturated bromine water to the combined filtrates and washings to reoxidize any iron that may have been reduced by the platinum, and boil the solution to expel all bromine. The volume of the solution at this point may conveniently be 250 ml. If sufficient hydrochloric acid to furnish 2 or 3 g. of ammonium chloride per 100 ml. on neutralization is not present, add pure solid ammonium chloride to bring the concentration up to this value. Add a few drops of methyl red indicator, and precipitate the hydrous oxides by carefully adding pure dilute (1 : 1) ammonium hydroxide to the boiling-hot solution until the color changes to yellow.[2] Allow the precipitate to settle for two or three minutes, and then filter immediately, using a coarse paper.[3] Wash the precipitate on the paper four or five times with hot 2 per cent ammonium chloride solution. It is not necessary to remove the precipitate quantitatively from the beaker. Replace the beaker containing the filtrate by the original beaker, and pour hot 1 : 1 hydrochloric acid through the paper to dissolve all of the precipitate. Wash the paper a few times with hot water and reserve. Dilute the solution to 200 ml., heat to boiling, and reprecipitate the hydrous oxides with ammonium hydroxide as before. Place the reserved filter paper in the beaker containing the precipitate, disintegrate it thoroughly with the stirring rod, and then filter off the precipitate intermixed with the paper pulp. Wash the precipitate thoroughly with the ammonium chloride wash solution. (If much magnesium is known to be present, a second reprecipitation of the hydrous oxides may be advisable.) Transfer the precipitate, together with any obtained in the treatment described in the next paragraph, to the weighed platinum crucible containing the residue from the silica determination, and ignite over a Meker burner or a blast lamp, observing the precautions mentioned on page 327. Weigh to obtain the sum of Fe_2O_3, Al_2O_3, TiO_2, and P_2O_5. Reserve the residue.

---

a porcelain casserole can be used instead. If a platinum dish is used, add a few drops of alcohol before evaporating with hydrochloric acid.

[1] If the sample contains metals precipitable by hydrogen sulfide, they should be removed at this stage, before the ammonia precipitation is made. Igneous silicate rocks usually contain only negligible amounts of these metals, so that for them the hydrogen sulfide treatment may be omitted. Platinum introduced from the vessels need not be removed at this point by precipitation with hydrogen sulfide.

[2] In the presence of much iron, the precipitate first obtained must be allowed to settle after boiling a minute or two to aid coagulation. The color of the indicator will then be perceptible in the supernatant liquid, and more ammonium hydroxide can be added until the indicator changes color. Methyl red is used in preference to phenol red as indicator here to avoid precipitation of manganese (p. 70).

[3] An 11 cm. S. and S. No. 589, Black Band, or equivalent, filter paper is best.

Make the combined filtrates and washings from the ammonia precipitate slightly acid with hydrochloric acid, and evaporate nearly to dryness [1] in a large Pyrex beaker. Cool, and add an excess of nitric acid (allow at least 3 to 4 ml. of concentrated nitric acid for each gram of ammonium chloride). Warm the covered beaker gently until vigorous reaction ceases, evaporate to a few ml., and then dilute to about 100 ml. Add dilute ammonium hydroxide in very slight excess as above to the hot solution, and filter off any precipitate at once. Wash a few times with the hot ammonium chloride solution, dissolve in a little dilute hydrochloric acid, reprecipitate with ammonia, wash, and ignite the precipitate with the main ammonia precipitate. Reserve the combined filtrates for the determination of calcium and magnesium.

Fusion of the ignited mixed oxides with potassium pyrosulfate.

The fusion of the ignited ammonia precipitate with alkali pyrosulfate serves two purposes: (1) It converts the oxides into sulfates, which can then be dissolved, this being necessary preparatory to the determination of total iron and titanium in the joint precipitate; and (2) it affords a means of recovering the silica which escaped separation in the dehydration and which was then carried down by the hydrous oxide precipitate.[2]

Add 5 to 7 g. of pure anhydrous potassium pyrosulfate to the crucible containing the ignited oxide residue,[3] and heat to *slightly* above the melting point of the pyrosulfate, keeping the crucible covered. Fumes of sulfur trioxide should come off very sparingly, if at all. After twenty or thirty minutes increase the heat somewhat. There must be no spattering. When most of the residue has dissolved, which may take an hour, heat the crucible more strongly so that the bottom is at low redness, and continue until no more particles are visible in the melt. It is usually possible to see if any undissolved substance remains by letting the uncovered crucible cool in a good light. The fused mass becomes less opaque as it cools, and at one point becomes quite transparent.

---

[1] The treatment described in this paragraph may perhaps be omitted in all but the most exact analysis. The purpose of the treatment is to recover any aluminum or iron in the filtrates. If the precipitation has been properly made, no significant amount of these will be found. At the same time, however, advantage is taken of the opportunity offered of removing the large amounts of ammonium chloride present by heating with nitric acid (p. 248). Large amounts of ammonium salts are undesirable in the subsequent determination of calcium and magnesium, although in most cases their removal is not demanded.

If ammonium salts are not to be destroyed, set the combined filtrates and washings on the steam bath, acidify with hydrochloric acid, and evaporate to a volume of 200 to 250 ml. Then precipitate calcium as described on p. 745.

[2] Again attention is called to the fact that not all the silica remaining in solution is carried down by the ammonia precipitate. However, if two careful dehydrations with intervening filtration have been made and if the ammonia precipitate is large, the amount that escapes precipitation is negligibly small.

[3] It is preferable to transfer as much as possible of the oxide residue to another crucible (25 ml. capacity) and to dissolve what little remains in the first crucible by a brief fusion with an appropriately small amount of pyrosulfate, pouring the melt into the second crucible and making the main fusion in it. When this is done, it is possible to determine the loss in weight which the crucible containing the mixed oxides has undergone during the ignition at the high temperature; this loss should always be ascertained in accurate work. The loss in weight cannot be determined by weighing the cleaned crucible after the pyrosulfate fusion, because several milligrams of platinum are brought into solution by the usual pyrosulfate fusion.

In all but the most accurate work the pyrosulfate fusion can be carried out in a transparent fused-silica crucible. Only a negligibly small amount of silica is introduced by using such a crucible.

When the fusion is complete, allow the crucible to cool, and transfer its contents to a 250 ml. beaker (place the crucible on its side in the beaker if the melt cannot readily be removed). Add 75 ml. of water and 2.5 ml. of concentrated sulfuric acid, and warm until everything except a few flakes of silica has gone into solution.[1]

Filter off the silica on a small filter paper, and wash the paper well with hot water. Receive the filtrate and washings in a 250 ml. Erlenmeyer flask. Place the filter paper in a platinum crucible, ignite, weigh, moisten the residue with a drop of dilute sulfuric acid and a few drops of hydrofluoric acid, evaporate off the acids, ignite again, and reweigh. The loss in weight represents the recovered silica and is to be added to that previously found (p. 737). Fuse the small residue in the crucible with a little potassium pyrosulfate, cool, and dissolve the melt in a few milliliters of water containing a drop or two of sulfuric acid. Combine this solution with the filtrate in the flask and reserve for the determination of iron.

Total iron.

Either of the two following procedures may be used for the determination of total iron:

1. ***Volumetrically***, by titration of the reduced iron solution with potassium permanganate.

This method is slightly less exact than the succeeding one, but it is more rapid and is sufficiently accurate to be satisfactory in the great majority of cases. Vanadium is counted with the iron (see Note).

Ferric iron is conveniently reduced to the ferrous state by hydrogen sulfide.[2]

Pass washed hydrogen sulfide for one-half hour into the above sulfate solution of iron, aluminum, etc., having a volume of 100 ml. and containing 2.5 per cent by volume of sulfuric acid. Continue to pass hydrogen sulfide into the solution for ten to fifteen minutes as the solution is heated to boiling. Then allow the solution to cool with the gas still passing through it. Filter the solution through a filter crucible or a filter paper that has been washed with dilute sulfuric acid to remove oxidizable organic matter, and wash the precipitate of sulfur and platinum sulfide with hydrogen sulfide water acidified with a little sulfuric acid.[1] Add 15 ml. of 1 : 1 sulfuric acid to the filtrate, which should be contained in a flask of suitable size.[2] Pass carbon dioxide (free from oxygen and hydrogen sulfide) into the solution through a glass tube reaching to the bottom of the flask, heat the solution to boiling, and continue to boil for twenty minutes to expel all hydrogen sulfide. Test the steam issuing from the flask with lead acetate paper for the presence of hydrogen sulfide. Then cool the solution by placing the flask in water, meanwhile continuing the passage of carbon dioxide to prevent the entrance of air. Dilute the solution[3] to 150 ml. and titrate with standardized 0.05 N or 0.1 N potassium permanganate solution (p. 592). Reserve the titrated solution for the titanium determination.

---

[1] It seems probable that this procedure does not render all the silica present insoluble. For the most exact results it is best to evaporate the acidified solution to fumes of sulfur trioxide in a platinum dish. The liquid is then cooled, diluted with water, and the silica filtered off as above.

[2] Hillebrand and Lundell (*Applied Inorganic Analysis*, p. 303) prefer the use of sulfur dioxide for the reduction of ferric iron (in which case platinum must first be removed by hydrogen sulfide), because when hydrogen sulfide is used, stable compounds of sulfur (polythionic acids) are formed which are subsequently oxidized by potassium permanganate, leading to slightly high results; see G. E. F. Lundell and H. B. Knowles, J. Am. Chem. Soc. *43*, 1560 (1921). The positive errors amount to 0.1 to 0.3 mg. of Fe, according to Lundell and Knowles, when the reduction with hydrogen sulfide is carried out essentially as described here.

Alternatively, the reduced iron solution can be titrated with potassium dichromate, diphenylamine sulfonate being used as indicator. Any quadrivalent vanadium present will not interfere, but the titrated solution cannot then be used for the colorimetric determination of titanium.

NOTE:

Amalgamated zinc cannot be used for the reduction of iron because titanium would then also be reduced (p. 599). Stannous chloride cannot be used if titanium is later to be determined in the same solution and if a correction is to be applied for the vanadium present, since the exact state of oxidation of the latter at the time of titration is not known. The reduction must therefore be effected by the use of hydrogen sulfide or sulfur dioxide. Both of these reduce vanadium to the quadrivalent stage, and in the latter form the element is oxidized by potassium permanganate to the quinquevalent state. In the presence of vanadium the results for iron by this procedure will consequently be high unless a correction is applied. If vanadium has been determined separately, it may be assumed that it is all present in the hydrous oxide precipitate, and the equivalent amount of permanganate solution can be deducted. Usually the amount of vanadium present in a rock is so small that for most purposes it need not be determined and the correction can be left out of account.

Walden, Hammett, and Edmonds[4] have described the use of a silver reductor for the reduction of iron in hydrochloric acid solution to the divalent state, with the subsequent titration of the ferrous iron with ceric sulfate, phenanthroline-ferrous ion being used as indicator. Under these conditions iron can be determined directly in the presence of vanadium, titanium, and chromium. Titanium and chromium are not reduced by silver; vanadium is reduced to the quadrivalent state, but is not oxidized back to the quinquevalent stage by ceric sulfate in the solution of high acidity in which the titration is made.

---

[1] An opalescence in the filtrate, due to sulfur, may be disregarded.

[2] Preferably one employs a flask provided with a stopper carrying an inlet tube reaching nearly to the bottom of the flask, and an outlet tube. A rubber stopper should be avoided because organic matter may be extracted from it during the boiling. An all-glass wash bottle is an ideal vessel for this operation.

[3] It is advisable to test a drop of the solution on a spot plate or crucible cove for ferric iron with potassium thiocyanate solution.

[4] G. H. Walden, Jr., L. P. Hammett, and S. M. Edmonds, J. Am. Chem. Soc. *56*, 350 (1934).

2. *Gravimetrically*, by precipitation as hydrous ferric oxide after separation as sulfide in ammoniacal tartrate solution.

To the solution of the sulfates of iron, aluminum, etc., from which silica has been removed and which should have a volume of approximately 100 ml., add four or five times as much tartaric acid as the weight of oxides present, make alkaline with ammonium hydroxide (no precipitate should form), acidify with 1 : 2 sulfuric acid, and add 2 ml. in excess. Saturate the acid solution with hydrogen sulfide to reduce the iron and precipitate platinum, which is present as the result of attack of platinum vessels in the preceding operations. Filter off the platinum sulfide and sulfur, make the filtrate strongly ammoniacal, and pass in more hydrogen sulfide to be sure the precipitation of ferrous sulfide is complete. Filter off the ferrous sulfide on paper, keeping the filter well filled at all times to prevent oxidation of ferrous sulfide. Wash the precipitate with dilute ammonium sulfide solution containing a little ammonium tartrate (about 1 per cent) and then with 2 per cent ammonium chloride solution containing a little ammonium sulfide to remove all tartrate, which would otherwise prevent the complete precipitation of iron hydroxide later. (If the precipitate is large, or the most accurate results are desired in any case, it is advisable to dissolve and reprecipitate the ferrous sulfide.)

Pour dilute hydrochloric acid through the paper to dissolve the ferrous sulfide (cover the funnel with a watch glass), and wash the filter with hot dilute hydrochloric acid, receiving the filtrate and washings in a 250 ml. beaker. Heat the acid ferrous solution to boiling, add 1 ml. of concentrated nitric acid, and continue to boil for a few minutes to oxidize the iron to the ferric state (p. 320). Dilute the solution to 150 ml., and precipitate the iron by adding an excess of ammonium hydroxide. Now transfer the filter paper to the beaker, and disintegrate the paper with the stirring rod so as to form a pulp. Filter off the hydrous ferric oxide, and wash the precipitate a few times with hot water. Ignite the precipitate to ferric oxide (p. 322).

NOTE:

The above separation of iron as sulfide from the other elements of the ammonia precipitate is based upon the fact that none of these is precipitated by ammonium hydroxide in the presence of sufficient tartrate, owing to the formation of tartrate complexes. The complex with iron is, however, decomposed by sulfide, owing to the very slight solubility of ferrous sulfide in ammoniacal medium. The other elements do not form sulfides under these conditions and remain in solution. This method is excellent for the separation of iron from aluminum, titanium, zirconium, chromium, phosphorus, and vanadium, as well as from the rarer elements, beryllium, columbium, and tantalum.

Ferric oxide.

To obtain the content of ferric oxide, deduct the ferric oxide equivalent of the ferrous oxide subsequently determined (p. 746) from the total iron as ferric oxide.

Titanium.

For the small amounts of titanium usually occurring in rocks, the colorimetric method with hydrogen peroxide as reagent is the best (Weller's method).

Preparation of standard titanium solution. The standard titanium solution which is needed for the colorimetric comparison can be prepared from potassium fluotitanate, potassium titanium oxalate, or titanium dioxide. The first two compounds are well suited for the purpose, and directions will be given here for making up the comparison solution from them.

(a) *From potassium fluotitanate.* Weigh out 1.62 g. of pure $K_2TiF_6 \cdot H_2O$[1] into a platinum dish, add 50 ml. of 1 : 1 sulfuric acid, and evaporate nearly to dryness. Cool the dish, wash down the sides, add more sulfuric acid, again evaporate until most of the sulfuric acid has been removed, and repeat the operation once more to insure the complete expulsion of fluorine. It is very important that all the fluorine be expelled (Note 3). Make up the solution to 500 ml. after adding enough concentrated sulfuric acid to make its concentration at least 5 per cent by volume in the final solution. This solution will contain 1.00 mg. of TiO_2 per milliliter if the salt weighed out is pure and contains the proper amount of water of crystallization. It is best to standardize the solution by precipitating the titanium with ammonium hydroxide. Dilute 50 ml. duplicates of the diluted solution to 150 or 200 ml., and add an excess of ammonium hydroxide to the nearly boiling solution. Filter off the precipitate of $TiO_2 \cdot x\,H_2O$ on paper, wash with hot water, and ignite to TiO_2. From the weight of the ignited residue, calculate the TiO_2 content of the solution per milliliter.

(b) *From potassium titanium oxalate.*[2] Transfer 4.5 g. of pure $K_2TiO(C_2O_4)_2 \cdot 2\,H_2O$, obtained by recrystallizing the commercial product once or twice from water, and 8 g. of ammonium sulfate to a small Kjeldahl flask. Add 50 ml. of concentrated sulfuric acid, and heat the mixture gradually. Finally bring the liquid to the boiling point, and boil for ten minutes to destroy oxalic acid. Cool, pour the solution into 700 or 800 ml. of water, and dilute to approximately 1 liter. Standardize the solution as described in (a).

This method of preparing the standard titanium solution is to be preferred to the preceding method, because there is no possibility of the presence of deleterious fluoride.

The colorimetric comparison.

(a) *If total iron was determined volumetrically by titration with permanganate.*

To the solution which remains after the titration of iron with permanganate, add 10 ml. of concentrated sulfuric acid and then, after cooling,

---

[1] The salt can be purified by recrystallizing from water. Dried at 105°, the salt becomes anhydrous.

[2] The method described is that of W. M. Thornton, Jr., and R. Roseman, Am. J. Sci. *20*, 14 (1930).

5 ml. of pure 3 per cent hydrogen peroxide. Dilute the solution to 250 ml.[1] in a volumetric flask and mix well. Next prepare a peroxidized titanium comparison solution of approximately the same concentration as the unknown solution as follows: Nearly fill a 250 ml. volumetric flask with cold dilute sulfuric acid of approximately the same acid concentration as the test solution, add the same amount of hydrogen peroxide, and mix by swirling. Now add the standard titanium solution from a buret until after mixing the color intensity of the two solutions is *approximately* the same. Record the volume of standard solution taken. Make up the solution to the mark and mix well. Make the color comparison of the two solutions in a colorimeter as described on page 658.

(b) *If total iron was determined by precipitation as sulfide in ammoniacal tartrate solution.*

In this case determine titanium in a separate sample by proceeding as follows. Weigh out 0.3 to 0.4 g. of rock powder into a platinum crucible, mix with four times as much anhydrous sodium carbonate, and fuse (p. 406). Detach the cold cake from the crucible and leach thoroughly in a beaker with water (*ca.* 50 ml.). Then filter through a small paper filter, keeping as much as possible of the residue in the beaker. Wash the residue and the paper with 1 per cent sodium carbonate solution, and discard the filtrate and washings. Dissolve the insoluble material in the beaker and on the paper in 50 ml. of 1 : 20 sulfuric acid, transfer the clear solution to a 100 ml. volumetric flask, add 3 to 5 ml. of 3 per cent hydrogen peroxide, and make up to the mark with 1 : 20 sulfuric acid. After mixing, proceed with the color comparison as in (a).

NOTES:

1. The yellow to orange color given by acid titanium solutions with hydrogen peroxide is probably due to an ion such as $[TiO_2(SO_4)_2]^=$. The color of the oxidized solution is quite stable.

2. Vanadium and molybdenum also give colored solutions with hydrogen peroxide, but usually these are not present in sufficient amounts in rocks to interfere with the determination of titanium. Iron when present in large amounts is disturbing because of its color. If it is present to an extent greater than 10 per cent of Fe_2O_3 in the sample, its effect should be neutralized by adding approximately the same amount of iron salt to the diluted standard titanium solution or else by adding equal *small* amounts of phosphoric acid to both the unknown and standard solutions. With small amounts of iron the color effect need hardly be taken into account. Thus 0.1 g. of ferric oxide in 100 ml. of 5 per cent sulfuric acid solution gives the same color intensity as 0.2 mg. peroxidized titanium dioxide in the same volume, corresponding to an error of 0.02 per cent of titanium dioxide in a 1 g. sample.

3. Hydrofluoric acid bleaches the yellow color. Even traces of fluoride have a marked effect on the color and must not be present. Great care must be taken in preparing standard titanium solutions from potassium fluotitanate to expel all hydrofluoric acid by repeated fuming with sulfuric acid. Alkali sul-

---

[1] If the yellow color is very light, it may be advisable to concentrate the solution to 100 ml. by evaporation, adding more hydrogen peroxide to restore the color before making up to the mark. For rocks containing more than 0.5 per cent of TiO_2, the solution should be diluted to 500 ml.

fates reduce the intensity of the yellow color of peroxidized titanium solutions,[1] the effect being less marked the greater the concentration of sulfuric acid present. For small amounts of titanium the error from this source amounts to only − 3 per cent of the total TiO_2 present, if 100 ml. of the solution contain the equivalent of 6 g. of potassium pyrosulfate and 10 per cent by volume of concentrated sulfuric acid.

Phosphoric acid also exerts a bleaching effect.

4. Since the accuracy of a colorimetric method is in general not greater than ± 3 per cent, it is best to determine titanium gravimetrically when it occurs in amounts greater than 1 or 2 per cent (which happens rather rarely in the case of rocks). The best gravimetric method involves the precipitation of the element with cupferron (p. 76) in acid solution after removal of iron with ammonium sulfide in the presence of tartrate.[2] Zirconium is precipitated with the titanium, and its amount must be deducted if it is present in appreciable quantities.

Aluminum.

To obtain the weight of aluminum oxide in the main portion, deduct the weight of total iron as Fe_2O_3, TiO_2, P_2O_5 (determined later), and the small amount of silica recovered after the pyrosulfate fusion, from the weight of the ignited mixed oxide residue.[3]

In the most accurate work, the platinum in the mixed oxides should be determined and deducted. The platinum correction is found by igniting the washed platinum sulfide-sulfur precipitate obtained with hydrogen sulfide (p. 739) to metallic platinum and deducting from the weight of the ignition residue the loss in weight undergone by the platinum crucible in the pyrosulfate fusion, which is easily determined by weighing the clean crucible before and after the fusion. Most of the platinum in the hydrous oxide precipitate owes its introduction to the evaporation of the hydrochloric acid solution in platinum for the dehydration of silica; as already mentioned, platinum is slightly attacked by ferric iron in the presence of hot hydrochloric acid. Naturally the amount of platinum brought into solution in this way depends upon a number of factors, the chief of which is the amount of ferric iron present.[4]

Calcium.

Acidify the combined filtrates and washings from the ammonia precipitation (p. 738) with hydrochloric acid,[5] bring to the proper volume, precipitate calcium oxalate by adding ammonium oxalate solution and ammonium hydroxide, and filter (see p. 358). Dissolve the precipitate in dilute hydrochloric acid, and reprecipitate the calcium by adding ammonium hydroxide and a little ammonium oxalate to the hot diluted solution. Filter and wash with dilute ammonium oxalate solution (p. 360). Weigh the calcium as carbonate (p. 351) or oxide (p. 353), observing the precautions particularized in Chapter XXI.

---

[1] H. E. Merwin, Am. J. Sci. [4], *28*, 119 (1909).

[2] W. M. Thornton, Jr., *Titanium, with Special Reference to the Analysis of Titaniferous Substances*, p. 90, Chemical Catalog Co., New York, 1927.

[3] The following constituents should also be deducted if they are present and have been determined: ZrO_2, Cr_2O_3, V_2O_3, and the rare earth oxides.

[4] To give an idea of the magnitude of the platinum correction, the data obtained by V. A. Stenger (private communication) in an analysis of a peat ash may be given. A 1.1 g. sample of ash containing 2.9 per cent of Fe_2O_3 yielded 3.3. mg. of total platinum, of which 0.8 mg. was derived from the platinum crucible used in the pyrosulfate fusion, leaving 2.5 mg. as the amount introduced in the double evaporations in a platinum dish for the dehydration of the silica. This amount corresponds to approximately 0.2 per cent of the weight of the sample.

[5] If ammonium salts have been destroyed by evaporation with nitric acid, add an excess of 10 ml. of concentrated hydrochloric acid.

If the ignited residue is brown or green, indicating the presence of manganese, obtain a correction for the amount present (assume manganese to be present as Mn_3O_4) by dissolving the residue in dilute nitric acid and determining manganese colorimetrically by the periodate method (cf. p. 713). Usually so little manganese is carried down by the calcium oxalate that it may be safely neglected.

Strontium.

A method which has long been considered standard for the determination of strontium in rocks consists in dissolving the weighed calcium oxide (or carbonate) residue in nitric acid, evaporating the solution to dryness, heating the residue to 150° to expel all water, and extracting with absolute ethyl alcohol and ether to dissolve the calcium nitrate, leaving strontium nitrate behind. However, Noll[1] has shown that this method does not yield accurate results, and he recommends the method of Rawson,[2] slightly modified, in which the dry mixed nitrates are extracted with nitric acid of sp. gr. 1.445. Calcium nitrate is dissolved, but strontium nitrate is not; and a satisfactory separation of the two elements is thus effected. Since strontium is incompletely precipitated with calcium oxalate, it is necessary to add some pure calcium salt to the combined filtrates from the oxalate precipitation and to precipitate the added calcium as oxalate to recover most of the remaining strontium.

A more accurate method for strontium, in which barium can be determined at the same time, involves precipitation of barium and strontium as sulfates in alcoholic solution after decomposition of the rock sample with hydrofluoric and sulfuric acids. The sulfates are transformed into carbonates by fusion with sodium carbonate, these are dissolved in nitric acid, and calcium is removed by Rawson's method. Barium is then precipitated as the chromate. In the filtrate from the barium precipitation strontium is successively precipitated as carbonate and sulfate and weighed as the latter. For the details of the method, see the work of Groves.[3] Strontium may also be determined spectrographically.[4]

Magnesium.

Determine magnesium in the combined filtrates from the calcium oxalate by precipitation with ammonium phosphate (p. 371) or 8-hydroxyquinoline (p. 374). The latter method is suitable for rocks containing relatively little magnesium.

---

[1] W. Noll, Z. anorg. allgem. Chem. *199*, 193 (1931).
[2] S. G. Rawson, J. Soc. Chem. Ind. *16*, 113 (1897).
[3] A. W. Groves, *Silicate Analysis*, p. 138.
[4] W. Noll, Chem. Erde *8*, 507 (1934).

Most of the manganese of the sample will be precipitated with the magnesium ammonium phosphate or the magnesium hydroxyquinolate, and therefore the weighed residue in either case must be corrected for the manganese present. If the rock is low in manganese, it is usually sufficiently accurate to assume that all the manganese is coprecipitated with the magnesium ammonium phosphate and to deduct the weight of $Mn_2P_2O_7$ equivalent to the manganese content of the sample (see p. 755). If much manganese is present, or for the greatest accuracy in any case, determine it as described below.

A correction should also be applied for the small amount of calcium, and possibly barium, that the magnesium *pyrophosphate* residue contains. Proceed as follows: Transfer the weighed magnesium pyrophosphate to a small beaker and dissolve it in a little nitric acid. Add 3 ml. of 1 : 3 sulfuric acid and evaporate to fumes to expel all nitric acid. Add 15 ml. of water to the cold residue, stir to bring all soluble material into solution, and then add 70 ml. of 95 per cent ethyl alcohol (these amounts are suitable for quantities of magnesium pyrophosphate up to 0.3 g.). Allow to stand overnight, filter off the precipitate, and wash with a 15 : 70 mixture of water-alcohol. Dissolve the calcium sulfate in a small volume of dilute hydrochloric acid, and precipitate calcium with oxalate in the usual manner in as small a volume as possible. Ignite the washed calcium oxalate to calcium oxide. Find the true weight of magnesium pyrophosphate by deducting the weight of $Ca_3(PO_4)$ corresponding to the weight of calcium from the weight of the impure magnesium pyrophosphate.

Manganese may be determined in the combined filtrate and washings from the calcium sulfate precipitation as follows. Evaporate the alcoholic solution to fumes of sulfuric acid, cool, and add 20 ml. of 1 : 3 sulfuric acid and 10 ml. of nitric acid. Dilute to about 50 ml., add 0.2 g. of potassium periodate, boil for one minute, and keep hot for about five minutes. Cool the solution to room temperature, make up to 100 ml., and determine the manganese colorimetrically as described on page 756.[1]

DETERMINATIONS ON SEPARATE PORTIONS: FERROUS IRON, THE ALKALIES, WATER, PHOSPHORUS, MANGANESE, CARBON DIOXIDE, CHLORINE

Ferrous iron.

Method. The sample is brought into solution by treatment with hydrofluoric and sulfuric acids, special care being taken to prevent oxidation of the ferrous iron in the process; and the ferrous iron is then titrated with standard potassium permanganate or potassium dichromate solution.

Procedure. Weigh 0.5 g. of 100-mesh rock powder into a 30 ml. platinum crucible, or into a larger one, if such is available. Add 1 or 2 ml. of water and rotate to moisten the powder. Pour 10 ml. of 1 : 1 sulfuric acid into the crucible, cover, and heat nearly to boiling over a Tirrill burner (hood).[2]

---

[1] If magnesium was weighed as the hydroxyquinolate, transfer the dried residue to a porcelain crucible, and heat gently to burn off organic matter. Dissolve the residue in the mixed acids as above, adding a very little sodium bisulfite. Boil the solution to expel sulfur dioxide, and oxidize as before with periodate.

[2] One or two coils of platinum wire, if they are available, should be placed in the crucible to prevent bumping.

Now move the cover of the crucible to one side slightly, and carefully pour in 5 ml. of hydrofluoric acid. Replace the cover, heat the liquid to boiling without delay, and keep it boiling *gently* for ten minutes. The boiling must proceed uninterruptedly; protect the flame from drafts. While the sample is being decomposed, fill a 400 ml. beaker half-full of cold water, and add to it 15 ml. of 1 : 2 sulfuric acid and 10 ml. of saturated boric acid solution. By means of the tongs (which must not be of iron) quickly place the covered crucible in the beaker. Stir the liquid to cause the contents of the crucible to be distributed through the solution, and titrate at once with 0.03 N (or 0.05 N) standardized potassium permanganate or potassium dichromate solution. If the latter solution is used, add 10 ml. of 85 per cent phosphoric acid and 6 drops of diphenylamine sulfonate to the solution before titrating (p. 609).

After the titration examine the bottom of the beaker for any dark particles, which would be indicative of incomplete decomposition of the rock. If such are found, repeat the determination using a more finely ground sample.[1]

NOTES:

The determination of ferrous iron in silicates is beset with a number of sources of error, which render a very exact determination rather difficult. The following are the chief sources of error:

1. Oxidation of ferrous iron to ferric in the grinding of the sample and in the decomposition with hydrofluoric acid. Attention has already been called to the fact that when silicates are ground extremely fine, a sensible amount of the ferrous iron present may be oxidized by the air. Generally, a rock need not be ground to extreme fineness when it is to be decomposed in hot hydrofluoric acid solution. If the grinding is not prolonged over fifteen minutes, this error will usually not be of serious magnitude. Grinding under alcohol minimizes the air oxidation of iron, but this method rarely needs to be resorted to. More serious is the possibility of oxidation of ferrous iron during the decomposition with hydrofluoric acid. Fluorides form very slightly ionized complex ferric fluorides, and therefore in the presence of excess fluoride the oxidation potential of the ferrous-ferric iron system is lowered to such an extent that air oxidation becomes easy. Great care must be taken to exclude oxygen during the decomposition of the rock powder. After the decomposition has been effected, the fluoride can be made harmless, and the possibility of air oxidation during the titration thereby eliminated, by adding boric acid, which forms fluoboric acid; the latter is ionized only extremely slightly into fluoride in the presence of an excess of boric acid.[2] The boric acid performs the further useful

---

[1] The simple procedure given above will be found satisfactory for the determination of ferrous iron in most cases. It is possible to eliminate entirely the possibility of oxidation of the ferrous iron by the air by providing the crucible with a bakelite cover fitted with a delivery tube for leading in carbon dioxide, and a funnel for adding the hydrofluoric acid. With this apparatus the air can be expelled from the interior of the crucible before the hydrofluoric acid is added, and the titration can be made in the crucible itself after the decomposition, if it is sufficiently large. Such special apparatus has been described by L. A. Sarver, J. Am. Chem. Soc. *49*, 1472 (1927), and C. J. Schollenberger, J. Am. Chem. Soc. *53*, 96 (1931).

[2] O. L. Barneby, J. Am. Chem. Soc. *37*, 1481 (1915).

function of preventing the interference of manganous salt in the titration of ferrous iron with permanganate. Owing to the formation of slightly ionized manganic fluoride, potassium permanganate will react with the manganous ions formed in the oxidation of the iron with the result that the end point in the titration becomes evanescent, especially when large amounts of iron are titrated. The addition of boric acid effectually prevents the formation of manganic fluoride and affords a sharp color change at the end point. When potassium dichromate is used to titrate the ferrous iron, the difficulty last mentioned does not present itself; and boric acid need not be added on this account, but should, however, be present to prevent air oxidation during the titration. Phosphoric acid must then be added in order to obtain a sharp color change at the true end point (p. 608), with diphenylamine or diphenylamine sulfonate as indicator (p. 492).

2. The presence of sulfides, vanadium (as V^{III}), and organic matter. These lead to high results for ferrous iron. Iron pyrite (FeS_2) is so slightly soluble in the hydrofluoric-sulfuric acid mixture under the conditions that obtain in the decomposition that its effect may be neglected. Pyrrhotite [1] is soluble and will reduce ferric iron. The amount of sulfides in igneous rocks is generally so small that this source of error is usually negligible and may be left out of consideration. Vanadium in the lower stages of oxidation will be counted as ferrous iron, but again the error is minute in most cases. Organic matter if present is likely to be oxidized, more so by potassium permanganate than by dichromate.

3. The presence of metallic iron derived from the steel mortar. If proper care has been taken in the preparation of the sample, this error will be very small, if not entirely negligible.

4. Incomplete decomposition of certain silicates (tourmaline, staurolite, axinite, and others). Refractory silicates can be decomposed by fusion with sodium metafluoborate in an evacuated Pyrex tube. The melt may be dissolved in a hydrochloric acid solution of iodine monochloride and the resulting solution titrated with potassium iodate: [2]

$$4\,Fe^{++} + IO_3^- + 6\,H^+ + Cl^- \rightarrow 4\,Fe^{+++} + 3\,H_2O + ICl.$$

Sodium and potassium.

Method. The J. Lawrence Smith method of decomposition of the sample is most often used in determining the alkalies.[3] In this procedure sodium and potassium are brought into water-soluble form by heating the very finely divided powder with a mixture of calcium carbonate and ammonium chloride. The sintered mass is leached with water to extract the alkalies, and filtered. Silica, aluminum, magnesium, iron, etc. all remain undissolved, whereas much of the calcium goes into solution as hydroxide and chloride. Calcium is removed from the filtrate by precipitation with ammonium carbonate, sulfate is precipitated with barium chloride, and ammonium salts are removed by volatilization. The alkali chlorides are weighed, and then either potassium or sodium is determined by the usual methods in the mixture; the other alkali is calculated by difference.

---

[1] Pyrrhotite is ferrous sulfide with a variable amount of sulfur in solid solution. When treated with a nonoxidizing acid, it yields the excess sulfur as the free element. The composition of pyrrhotite approximates Fe_7S_8.

[2] M. H. Hey, Mineralog. Mag. *26*, 116 (1941); H. P. Rowledge, J. Roy. Soc. W. Australia *20*, 165 (1934).

[3] J. Lawrence Smith, Am. J. Sci. [2] *50*, 269 (1871).

Procedure. The sample must be very finely ground, or else it is certain that the decomposition will be incomplete.[1] Weigh out roughly 0.5 g. or slightly more of 100-mesh powder, and grind it exceedingly fine in an agate mortar. Transfer the powder to a weighing bottle, and weigh out 0.5 g. of sample into a platinum basin or a 100 ml. porcelain casserole. Mix 0.5 g. of pure ammonium chloride very thoroughly with the powder, using a small agate pestle. Weigh out, to the nearest decigram, 4 g. of calcium carbonate low in alkalies[2] on a watch glass; and add three fourths of this, a little at a time, to the vessel containing the sample, mixing with extreme thoroughness.[3] Do not apply heavy pressure on the pestle, to avoid scratching the vessel. When the mixing is complete, lay the pestle down in the watch glass containing the remainder of the calcium carbonate, and transfer the mixture with the aid of a spatula to a J. Lawrence Smith crucible[4] (Fig. 131) or an ordinary 30 ml. platinum crucible. It is advisable to place a little calcium carbonate in the bottom of either crucible to prevent adhesion of sintered material at the end of the ignition. If a Smith crucible is used, first transfer the powder to a creased piece of glazed paper, and thus avoid the possibility of loss in filling the crucible. Pour the carbonate remaining on the watch glass into the dish, and rub it over the inside with the pestle to remove any small amount of adhering powder, and finally transfer the whole to the crucible.

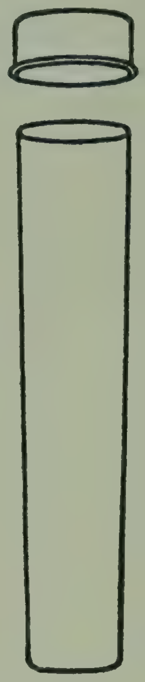


Fig. 131. J. Lawrence Smith crucible.

If a Smith crucible is being used, insert it in a nearly vertical asbestos or transite board with a hole of suitable size to fit the crucible tightly about one fourth of the distance from the capped end. If an ordinary crucible is employed, place it in a hole in a square of asbestos. About one third of the crucible should extend below the asbestos. These asbestos shields must be used to prevent the possible loss of alkali chlorides by volatilization in the subsequent strong heating. Cap or cover the crucible, and place a 50 ml. beaker containing water on the top of the cover of the ordinary crucible. Heat the crucible not above redness with a low flame for ten to fifteen minutes or until ammonia ceases to come off. Reduce the heat if ammonium chloride fumes appear. Then increase the heat until the lower third of the crucible is bright red. The finger-form crucible may be heated with the full flame of a Tirrill or Meker burner. Continue the heating for about three quarters of an hour. Allow the crucible and its contents to cool, add enough water to the residue to cover it, allow to stand for a few minutes, rinse off the cover, and then wash the residue into a silica dish or small porcelain casserole. Or, in the case of the Smith crucible, tap the inverted crucible to make the sintered mass fall out into the dish. Add enough water to the residue in the dish to give a volume of 50 to 75 ml., and grind up the mass with a small agate pestle until no lumps remain. Then heat the liquid to boiling and keep at the boiling point for a few minutes. Decant the solution through a fast-filtering paper, leaving as much as possible of the residue in the dish; receive the filtrate in a 400 ml. Pyrex beaker or, better, a large silica dish. Add 50 ml. of hot water to the dish or casserole, heat to boiling, rub the insoluble mass with the pestle for some minutes, and again decant. Repeat the last operation three more times. Wash the paper with 50 ml. of hot water or, preferably, 50 ml. of hot saturated calcium hydroxide solution. Test the residue in the dish for complete decomposition by treating a portion of it with dilute hydrochloric acid. All should dissolve except possibly a few specks of iron ore minerals.

---

[1] According to M. O. Lamar, W. M. Hazel, and W. J. O'Leary, Ind. Eng. Chem., Anal. Ed. 7, 429 (1935), refractory samples can be decomposed in one treatment if reduced to 200-mesh powder; 100-mesh powder may not be completely decomposed.

[2] This is best prepared by precipitating a dilute solution of calcium chloride (from purest calcium carbonate and hydrochloric acid) at boiling temperature with excess ammonia and ammonium carbonate. The precipitate should be well washed with hot water and reserved especially for alkali determinations in silicates.

[3] Alternatively, the sample may be mixed with a previously prepared, finely ground mixture of calcium carbonate and ammonium chloride (obtained, for example, by grinding the two together in a ball mill).

[4] A Smith crucible is to be preferred for the decomposition because in it the sample can be heated to a high temperature without danger of loss of alkalies by volatilization. However, an ordinary crucible will give perfectly satisfactory results if a little care is exercised in the heating.

Add a few ml. of concentrated ammonium hydroxide to the solution in the beaker, and then precipitate calcium by adding an excess of ammonium carbonate (2 g. in 25 ml. of cold water) to the warm solution. Heat the solution to boiling and allow the precipitate to settle. Filter the solution through paper into a large porcelain casserole or silica dish, wash the precipitate carefully with hot water,[1] and evaporate the filtrate to dryness on the steam bath.

Carefully heat the dried residue to expel ammonium salts, taking care not to volatilize the alkali chlorides by too strong heating.[2] The residue will be dark-colored, but this does not matter. Dissolve it in 5 ml. of water, add one drop of 10 per cent barium chloride solution, and allow to stand for a few minutes. Then add a few drops of ammonium hydroxide and one ml. of cold saturated ammonium carbonate solution, and evaporate to dryness on the steam bath. Take up the residue in a few ml. of cold water, and filter through a small filter into a 30–35 ml. platinum crucible or small platinum dish. Wash the dish and paper carefully with small portions (2 to 3 ml.) of warm water containing a drop each of ammonium hydroxide and saturated ammonium carbonate solution in 20 ml.; 20 to 25 ml. of water will be sufficient for washing. Evaporate the filtrate and washings to complete dryness on the steam bath. Heat the crucible (or dish) very carefully (just below redness) to expel ammonium salts, keeping the crucible covered at first to prevent possible loss of solid by decrepitation. Cool, moisten the residue with a drop of dilute hydrochloric acid, and rinse off the cover if any particles adhere to it. Evaporate to dryness, taking the same precautions as before, and heat the residue until the alkali chlorides just begin to melt in places. Cool the crucible and weigh. Reheat to incipient fusion of the chlorides and weigh again, repeating the process, if necessary, until constant weight is obtained. Then dissolve the salts in 5 to 10 ml. of hot water, filter to remove any insoluble material, and wash the paper, ignite it in the crucible, and weigh to obtain the weight of the insoluble material.

---

[1] In the most exact work the calcium carbonate should be dissolved in hydrochloric acid and reprecipitated with ammonium carbonate to recover any small amounts of alkali chlorides coprecipitated.

[2] It will be easier to expel ammonium salts if the operation is carried out in a small, preferably platinum, dish. Therefore when the solution has been reduced to a small volume, transfer it to a platinum dish and complete the evaporation in it.

Dilute the solution of the alkali chlorides to 100 ml. in a volumetric flask, mix, and transfer 25 ml. to a 50 ml. Pyrex beaker. Evaporate the solution nearly to dryness, and determine sodium as described on page 416, with zinc uranyl acetate.[1] Calculate potassium by difference, after correcting the sodium for the amount found in the blank. In running the blank, weigh out the same amounts of ammonium chloride and calcium carbonate as used in the determination itself, and follow all the steps of the determination as closely as possible.

NOTES:

1. The active reagents in the J. L. Smith method of silicate decomposition are calcium oxide and calcium chloride. The ammonium chloride in the decomposition mixture furnishes calcium chloride by interaction with the calcium carbonate:

$$CaCO_3 + 2\,NH_4Cl \rightarrow CaCl_2 + 2\,NH_3 + CO_2 + H_2O.$$

Calcium oxide (from the excess calcium carbonate) and chloride, acting jointly on the silicate at the high temperature, displace the alkalies from the silicate, forming alkali chlorides. The calcium-rich silicate formed is insoluble in water, so that when the sintered mass is leached with water only the alkali chlorides and the excess calcium chloride and hydroxide (from the calcium oxide) dissolve. Magnesium would be likely to dissolve to some extent were it not for the presence of calcium hydroxide in the solution, which precipitates magnesium hydroxide. Boron, molybdenum, and some fluorine accompany the alkali metals; and when present in appreciable amounts, they must be removed by appropriate treatment.[2] Lithium is partially retained in the leached residue, and some of it is lost in the precipitation of calcium carbonate. Since the reaction mixture does not fuse, it is highly important to have the reactants present in a very fine form and intimately intermixed, or else decomposition may be incomplete. When much iron is present in the sample, the mixture may partially fuse, and the mass will then be hard to remove from the crucible. This difficulty can be avoided by increasing the proportion of calcium carbonate in the reaction mixture.

Calcium chloride alone can be used to decompose silicates.[3]

It appears to be advantageous to use a mixture of calcium carbonate and calcium chloride directly in the silicate decomposition as recently proposed by Van Tongeren,[1] who gives the following directions. The sample is weighed into an agate mortar, a solution of calcium chloride prepared by nearly neutralizing 0.5 g. of pure calcium carbonate with hydrochloric acid is added, and the sample is then ground for some minutes under this solution. Then there is added, with intervening mixing, most of a portion of 4 g. of calcium carbonate. Alcohol is added gradually to give the mass a doughlike consistency. The mixture is then transferred by means of a spatula to the crucible (either the ordinary or J. L. Smith form), the bottom of which has been covered with a thin layer of calcium carbonate, and the mortar is rinsed with the remainder of the calcium carbonate. The crucible is placed in a drying oven; and when the contents are dry, the crucible is heated directly to the decomposition temperature. The purpose of weighing the sample before grinding is to avoid possible weight changes due to the taking-up of water from the atmosphere and possible oxidation of ferrous iron. By grinding under liquid in the manner described, there is no danger of loss of powder, and much less time is required than when the sample is ground in the dry state.

---

[1] Alternatively potassium can be determined as described on p. 413 and sodium found by difference, or else the solution of the mixed chlorides can be divided into two parts and both sodium and potassium determined directly.

[2] See Lundell and Hoffman, *Outlines of Methods of Chemical Analysis*, p. 76.

[3] E. Mäkinen, Z. anorg. Chem. *74*, 74 (1912).

Stevens[2] has proposed the use of barium chloride in place of ammonium chloride in the J. L. Smith method. The mixture may then be heated more rapidly, the alkali metal chlorides are obtained free from sulfate, and samples high in sulfate (alunite) do not yield a fused mass as in the usual method. The accuracy of the new procedure is equal to that of the old.

2. Before the advent of the Smith procedure, silicates were generally decomposed by the Berzelius method for the determination of the alkalies. In this method the sample is heated with hydrofluoric and sulfuric acids, the excess of hydrofluoric acid is expelled, the residual sulfates are brought into solution and transformed into the chlorides by precipitation with excess barium chloride.[3] Magnesium is precipitated with barium hydroxide, and the excess of barium, iron, aluminum, calcium, etc. is removed with ammonium hydroxide and ammonium carbonate.

Potassium may be determined directly in a silicate by decomposing the latter with hydrofluoric and perchloric acids, steam-distilling to remove all fluorine (aluminum fluoride is not completely decomposed by fuming with perchloric acid), and separating potassium perchlorate in the usual manner (page 414).[4]

When the quantity of silicate available is limited, as often happens in mineral analysis but hardly ever in rock analysis, it may be necessary to determine all constituents, as far as possible, in one portion of sample. In such cases decomposition of the silicate is effected by fusion with boric oxide (Jannasch), lead oxide, or bismuth oxide. For general use these fluxes are undesirable.

✓ **Water.**

Regarding the condition of water in rocks, see page 137. The influence of fine grinding upon the water content has already been discussed (p. 240).

---

[1] W. van Tongeren, Chem. Weekbl. *32*, 224 (1935).

[2] R. E. Stevens, Ind. Eng. Chem., Anal. Ed. *12*, 413 (1940).

[3] If sodium alone is to be determined (triple-acetate method), sulfate need not be removed.

[4] H. H. Willard, L. M. Liggett, and H. Diehl, Ind. Eng. Chem., Anal. Ed. *14* 234 (1942).

Hygroscopic water (H_2O −). Hygroscopic water corresponds more or less to "nonessential" water (p. 136). It is determined by finding the loss in weight of the sample when dried at 105° or 110°.

Procedure. Weigh 1 g. of powder into a platinum crucible[1] and dry at 105° to 110° in an oven for thirty or forty-five minutes. Repeat the heating at thirty-minute periods until constant weight is attained.

Combined water (H_2O +). For the determination of combined water in silicate rocks the method of Penfield[2] gives very satisfactory results. In this simple direct method for water, the rock powder is strongly heated in a long glass tube closed at one end. When the water has all been expelled and condensed on the sides of the tube, the portion of the tube holding the powder is softened in the flame and drawn off. The tube now holding the water alone is weighed; then the water is driven out by heating and aspiration, and by weighing the empty tube the weight of total water is found by difference. Combined water is obtained by deducting hygroscopic water from the total.

Procedure. There will be needed a tube of Pyrex from 15 to 20 cm. in length with an internal diameter of 5 or 6 mm. and closed at one end. It is advisable that the tube have an enlargement about half-way from the end.

First dry the tube by drawing air through it by means of a narrow tube reaching to the bottom while heating gently with a burner. Cool and weigh. With the aid of a short dry thistle tube introduce from 0.5 to 1.0 g. of rock powder into the bottom of the tube. Withdraw the thistle tube carefully to avoid leaving any trace of powder on the walls of the tube, and reweigh. Tap the horizontal tube lightly to form a free space above the powder to permit the water vapor to escape later without possibly blowing powder towards the open end of the tube. Support the tube in a nearly horizontal position in a clamp, inclining it very slightly toward the open end. Wrap a narrow strip of cloth or filter paper around the bulb and a few centimeters beyond toward the open end. Keep this cloth moist during the subsequent heating by dropping cold water upon it at intervals. Care must of course be taken to prevent water from running down the outside of the tube towards the open end.

With the burner in the hand, begin to heat the sealed end of the tube gently. Gradually increase the heat to the full flame of a Meker burner (or use a blast lamp). Rotate the tube slowly to keep the red-hot glass from sagging. Continue to heat strongly for fifteen minutes. Then drive into the bulb any water that has condensed between the closed end and the bulb by heating this section of the tube very gently with a small flame. Then apply the flame about half-way between the closed end of the tube and the bulb, and while rotating the horizontal tube draw off the part containing the powder.[3] There must be no powder in the section of the tube containing the water. Round off the sealed end of the long tube if a thread of glass remains, and allow it to cool, keeping it horizontal and covered with the moist cloth. Reject the sealed-off end of the tube containing the sample.

---

[1] A porcelain crucible may be used if the dried sample is not to be used for any other determination later.

[2] S. L. Penfield, Am. J. Sci. [3] *48*, 30 (1894). The method was first used by G. J. Brush.

[3] The closed end of the tube is held with a pair of tongs, or else a short piece of glass tubing is fused to the end to serve as a handle. A blast lamp is conveniently used here

When the tube has come to room temperature, remove the moist cloth and carefully dry the outside of the tube with a lintless cloth. Then weigh it. Next replace the tube in the clamp, heat gently, and draw off the water vapor by means of a narrow glass tube inserted to the bottom and connected to the suction line. When the tube is dry, allow it to cool, and reweigh. The decrease in weight gives the total water. Deduct the amount of hygroscopic water to obtain the combined water.

NOTES:

1. The above procedure gives good results in the absence of minerals which lose all their water at high temperatures only. It gives satisfactory results even with rocks containing much carbonate; in this case the tube containing the water is inclined, mouth down, to effect displacement of the carbon dioxide by air. A correction is then applied for the water vapor carried away by the carbon dioxide.

In the determination of water in minerals which tenaciously retain it at high temperatures ($> 1000°$) [1] or which give off sulfur oxides and other volatile constituents, a flux must be used to decompose the sample and retain the volatiles. For this purpose lead oxide (with or without lead dioxide),[2] lead chromate, sodium carbonate, and other substances have been used. Lead chromate (m. p. 844°) has recently been recommended.[3] When it is used, water can be determined in samples containing halogens, sulfate, sulfide, and ferrous iron. Iron in the ferrous state reduces water to hydrogen at high temperatures·

$$2\,FeO + H_2O \rightarrow Fe_2O_3 + H_2.$$

The presence of an oxidizing agent such as chromate prevents this reaction. Lead chromate may be used either in the Penfield method oı in the direct method involving the absorption of the expelled water in a tube containing a desiccant (p. 301). For details of the latter method consult the works of Groves or Hillebrand-Lundell already cited.[4]

Water may also be determined volumetrically (p. 305) in silicates after expulsion by strong heating.[5]

2. The old method of determining total water by obtaining the loss in weight after ignition gives only approximate results. On the one hand, volatile constituents other than water, such as carbon dioxide, sulfur, and chlorine, may be driven off, and, on the other hand, oxidation may increase the weight of the residue. Ferrous iron especially will lead to low results for the last reason.

---

[1] Among the minerals requiring a very high temperature for the complete expulsion of water are mica, tourmaline, topaz, epidote, staurolite, and talc. See, for example, A. F. Smethurst, Mineralog. Mag. *24*, 173 (1935).

[2] E. Dittler and H. Heuber, Z. anorg. allgem. Chem. *195*, 50 (1931).

[3] M. Hartwig-Bendig, Z. angew. Mineral. *3*, 195 (1941).

[4] See also M. Dittrich and W. Eitel, Z. anorg. allgem. Chem. *75*, 373 (1912); *77*, 365 (1912); *78*, 191 (1912).

[5] E. Dittler and H. Heuber, Z. anorg. allgem. Chem. *195*, 41 (1931); *199*, 17 (1931).

Phosphorus.

Method. The sample is decomposed with nitric and hydrofluoric acids, and any silica remaining after this treatment is rendered insoluble by heating. The residue is boiled with nitric acid to bring all the phosphorus into solution as orthophosphate, and the solution is filtered. In the filtrate phosphorus is precipitated as ammonium phosphomolybdate. The precipitate may be weighed after drying at 110°, or, better, ignited to $P_2O_5 \cdot 24\ MoO_3$, or else dissolved and phosphorus precipitated as magnesium ammonium phosphate, which is then ignited to magnesium pyrophosphate. Since the amount of phosphorus present is nearly always very small, weighing the ignition product $P_2O_5 \cdot 24\ MoO_3$ is entirely satisfactory.

Procedure. Weigh 0.5 g. of powder into a small platinum dish or a large platinum crucible. Add 5 ml. of water, 3 ml. of concentrated nitric acid, and 5 ml. of hydrofluoric acid. Stir the mixture with a platinum wire, or swirl the liquid carefully to wet all the powder. Evaporate to dryness on the steam bath or in a radiator (p. 184). Add 1 ml. of concentrated nitric acid to the residue and evaporate to dryness again; repeat the evaporation with nitric acid once more, or preferably twice more, to insure decomposition of fluorides. Heat the dish or crucible over a flame until the residue becomes slightly brown. Cool, and add 10 ml. of 1 : 3 nitric acid. Boil the solution for a few minutes, and filter through a small paper into a 150 ml. beaker. Wash the residue with hot 1 : 3 nitric acid, keeping the volume below 40 ml. Precipitate the phosphorus in the solution by the addition of ammonium molybdate reagent, as described on page 714, using proportionately smaller volumes. Allow the liquid to stand for a few hours, and then collect the yellow precipitate in a weighed Gooch or porcelain filter crucible, and wash with acid ammonium nitrate solution (40 to 50 ml. should be sufficient). Heat the precipitate at a low temperature (100°) until dry, then place the crucible in a furnace, and heat slowly to 450° and keep at this temperature for fifteen or twenty minutes. In the absence of a furnace, place the crucible in a capsule or ordinary porcelain crucible, and heat the latter at dull redness until the entire precipitate has become uniformly greenish-black in color. Do not heat above low redness. Cool, weigh, and repeat the ignition to constant weight. The ignited residue has the composition $P_2O_5 \cdot 24\ MoO_3$.

If much vanadium is present in the rock — which rarely happens — the ammonium phosphomolybdate precipitate will be contaminated with ammonium vanadomolybdate, and high results will be obtained for phosphorus.

Manganese.

Method. For the small amounts of manganese found in rocks, the colorimetric method of determination is most suitable. The rock powder is decomposed with hydrofluoric and sulfuric acids. Any insoluble material is filtered off after the expulsion of excess hydrofluoric acid, and manganese is oxidized to permanganate in the acid filtrate by potassium periodate or other suitable oxidizing agent. The concentration of manganese in the oxidized solution is determined colorimetrically by comparison with a solution of known permanganate concentration.

Procedure. To 0.5 g. of rock powder in a large platinum crucible add 5 ml. of 1 : 1 sulfuric acid and 5 ml. of hydrofluoric acid. Rotate the crucible to mix the contents. Place the crucible in a radiator, and heat carefully at first and then more strongly until fumes of sulfur trioxide appear in abundance. Cool, add 2 to 3 ml. more of sulfuric acid, and evaporate until most of the sulfuric acid has been driven off. To assure the expulsion of all the hydrofluoric acid, add another 2 to 3 ml. portion of 1 : 1 sulfuric acid and evaporate nearly to dryness. Add 10 to 15 ml. of 1 : 5 sulfuric acid to the residue, warm somewhat, stir up the insoluble matter, and filter it off on a small filter paper, using a 100 ml. flask to receive the filtrate. Wash the residue with hot water, keeping the total volume of filtrate and washings below 50 ml.

To the solution add 3 ml. of sulfuric acid and 1 ml. of 85 per cent phosphoric acid, and then 0.2 to 0.3 g. potassium periodate.[1] Heat to boiling and keep at the boiling temperature for five minutes, cool, transfer the solution to a 100 ml. volumetric flask,[2] and dilute with water to the mark. After mixing, compare the color intensity with that of a standard permanganate solution, preferably using a colorimeter (p. 658). Prepare the standard manganese solution in the following manner. Measure out accurately into a beaker a sufficient amount of standardized potassium permanganate solution to furnish approximately the equivalent of 0.05 g. of MnO. Add 75 ml. of 1 : 4 sulfuric acid and then dropwise a solution of chloride-free sodium sulfite until the solution is decolorized. Boil to expel sulfur dioxide, add 1 g. of potassium periodate, keep at the boiling point for five or ten minutes, cool, and dilute the solution to 500 ml. in a volumetric flask. There is thus obtained a stable standard permanganate solution containing the equivalent of 0.1 mg. MnO per milliliter; the exact strength is calculated from the normality and volume of potassium permanganate taken. To obtain a comparison solution showing approximately the same color as the diluted unknown, measure out into a 100 ml. flask three-fourths filled with 1 : 20 sulfuric acid [3] enough standard solution to match roughly the color of the test solution. Then make up to 100 ml., mix, and make the color comparison exactly. There should not be more than about 2.5 mg. of MnO per 100 ml. of solution, or else the color is likely to be too dark for satisfactory comparison.

Carbon dioxide.

Before determining carbon dioxide, it is advisable to test the sample for carbonates by warming the powder with dilute hydrochloric acid and noting whether there is any liberation of carbon dioxide.

Procedure. Take a 2–3 g. sample of powder and proceed as described on page 385.

---

[1] If potassium periodate is not available, use sodium bismuthate or ammonium persulfate to oxidize manganese to permanganate, basing the procedure on the directions given on p. 710 or p. 712.

[2] Or to a 200 or 250 ml. volumetric flask if the color intensity is great.

[3] This acid must be free from reducing substances. If necessary add dilute permanganate to it to impart a very faint pink color, and reserve especially for the colorimetric manganese determination.

Chlorine.

Procedure. Fuse 1 g. of rock powder with 5 g. of chloride-free sodium carbonate, leach the melt with hot water, filter, wash with 1 per cent sodium carbonate solution, acidify the filtrate with nitric acid,[1] and precipitate the chloride with silver nitrate (p. 312). Filter off the silver chloride in a filter crucible, wash the precipitate with water acidulated with nitric acid, and dry at 110°–150°.

DETERMINATION OF BARIUM, ZIRCONIUM, SULFUR, AND CHROMIUM

These elements are all determined in one portion

Method.

The sample is fused with sodium carbonate and a little potassium nitrate. The oxidizing fusion serves to convert sulfidic sulfur into sulfate, and trivalent chromium into chromate. The melt is extracted with water, treated with a little alcohol to reduce manganate, and the mixture filtered. The following principal elements go into the filtrate: *sulfur*, *chromium*, silica in part, aluminum in part, phosphorus, and vanadium. The residue contains *barium*, *zirconium*, silica in part, aluminum in part, nearly all of the iron, titanium, manganese, calcium, magnesium, the rare earths, etc.

Chromium can be determined in the filtrate by colorimetric comparison with standard potassium chromate solution, and sulfate by precipitation in acid solution by barium chloride without prior removal of silica.

The water-insoluble residue is digested with sulfuric acid to precipitate barium sulfate (together with any strontium sulfate and some calcium sulfate), which is weighed after purification. The filtrate from the barium sulfate is strongly acidified with sulfuric acid, hydrogen peroxide is added to keep titanium in solution, and zirconium is then precipitated as the phosphate, ignited to the pyrophosphate, and weighed as such.

Decomposition of the sample.

Mix 1 g. of sample with 5 g. of sodium carbonate (as free as possible from sulfate) and 0.2 g. of potassium nitrate, and fuse in a platinum crucible over a Meker burner. The crucible should be placed in an asbestos board, preferably slightly inclined to prevent the entrance of sulfur compounds from the flame. Heat carefully at a low temperature at first, and then strongly. When decomposition is complete, remove the flame, allow the crucible to cool somewhat, then grasp it with the tongs, and distribute the melt in a thin shell over the interior walls by imparting a slow rotatory motion to the crucible as it cools. Transfer the cooled melt to a 250 ml. beaker, add 50 to 75 ml. water and a few drops of alcohol, and digest on the steam bath until disintegration is complete and manganate is reduced. Disintegration of the melt can be hastened by breaking it up, during the digestion, with a glass rod flattened at one end. Then filter, keeping as much as possible of the insoluble matter in the beaker. Wash the residue well with a 1 per cent solution of sodium carbonate. Reserve the filtrate and washings for the determination of chromium and sulfur, and examine the residue for barium and zirconium.

---

[1] If the solution is not perfectly clear after acidification, filter.

Barium.

Without removing the paper from the funnel, wash whatever residue is on it into the beaker containing most of the residue, dilute the mixture to 75 ml., add 2 ml. of concentrated sulfuric acid and a few drops of sulfurous acid, and warm gently until all has dissolved except the barium sulfate. Allow the solution to stand for an hour at room temperature, and then filter off the barium sulfate on a small paper. Wash the precipitate with cold water. Reserve the filtrate and washings for the determination of zirconium.

The barium sulfate thus obtained will contain calcium sulfate, and also strontium sulfate if strontium is present, and it must therefore be purified as follows. Ignite the paper with its precipitate in a platinum crucible, add 0.5 g. of sodium carbonate, heat to fusion, and keep at this temperature for ten minutes. Leach the melt with cold water, and filter off the residue on a small filter paper. Wash the residue well with cold water, and then dissolve it on the paper in a few drops of dilute hydrochloric acid. Wash the paper thoroughly, catching the hydrochloric acid solution of the barium and the washings in a 250 ml. beaker. Dilute the solution to 100 ml., and precipitate the barium in cold solution by adding 10 ml. of 1 : 5 sulfuric acid. Filter off the precipitate after one or two hours, wash with cold water, ignite (p. 341) and weigh the barium sulfate.

NOTE:

When appreciable amounts of strontium are present, much of it is left with the barium sulfate after the "purification."

Zirconium (including hafnium).

To the filtrate from the first barium sulfate precipitate add enough sulfuric acid to make the concentration approximately 10 per cent by volume of the concentrated acid. Add 5 ml. of 3 per cent hydrogen peroxide (to keep titanium in solution), and warm the solution to about 50°. Precipitate the zirconium by adding 1 g. of diammonium phosphate dissolved in 10 ml. of water. Allow the liquid to stand not less than two hours before filtration, adding more hydrogen peroxide if the yellow color of the titanium fades. Filter through a small filter paper, and wash the precipitate with a cold 5 per cent solution of ammonium nitrate. Discard the filtrate.[1]

Ignite the precipitate in a platinum crucible, applying the full heat of a Meker burner for ten minutes. The ignition residue consists of ZrP_2O_7.

---

[1] The rare earth elements, if present, will be found in the filtrate and can be determined therein by a method devised by Hillebrand. See W. F. Hillebrand, *Analysis of Silicate and Carbonate Rocks*, p. 176, or W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*, p. 755.

NOTE:

The above procedure for the determination of zirconium was worked out by Lundell and Knowles.[1] The precipitation of zirconium phosphate is best made in the presence of much sulfuric acid to prevent contamination by titanium and other elements. Precipitation is quantitative even in solutions containing as much as 20 per cent by weight of sulfuric acid. The precipitate is thought to have the composition $ZrH_2(PO_4)_2$. A 10- to 100-fold excess of precipitant should be used, the larger amount when only a little zirconium is present. On prolonged washing the precipitate loses phosphorus as the result of hydrolysis, and slightly low results are obtained. With the small amounts of zirconium found in silicate rocks, this source of error is negligibly small.

Chromium.

If the filtrate from the water-insoluble residue of the sodium carbonate fusion is yellow, chromium is present. If desired, it can be determined by concentrating the solution to 50 ml. and comparing the color with a solution of potassium chromate. This can be done very simply as follows. Pour the test solution into a 50 ml. graduate or Nessler tube. To another similar 50 ml. graduate containing the same volume of water, add 1 g. of sodium carbonate, and then add dropwise, with stirring, a dilute solution of potassium chromate of which 1 ml. is equivalent to 0.2 mg. Cr_2O_3, until the colors match when the columns of liquid are viewed from above against a white background. Even if the determination of chromium is not made, the absence or presence of a yellow color in the solution should be noted and reported.

Total sulfur.

Whether or not chromium was determined by colorimetric comparison, dilute the filtered water extract of the sodium carbonate melt to 150 or 200 ml., add a few drops of methyl orange solution, and slowly pour in dilute hydrochloric acid until the liquid is acid, keeping the beaker covered to prevent loss as a result of the evolution of carbon dioxide. Heat the solution nearly to boiling, and add 25 ml. of 2 per cent barium chloride solution to precipitate the sulfate. Allow the solution to cool to room temperature, and let it stand for one or two hours. Filter off the precipitate on a small filter paper, and wash with cold water. Ignite the barium sulfate in a weighed platinum crucible, cool, moisten the residue with a drop of dilute sulfuric acid and a few of hydrofluoric acid, evaporate, and again ignite (p. 341). Report the total sulfur present as S. For the most accurate results a blank should be run through all the steps of the procedure.

NOTES:

1. Sulfur occurs in rocks in the form of both sulfate and sulfide. The oxidizing fusion converts sulfides to sulfates, and therefore total sulfur is obtained in the procedure described. In the absence of knowledge regarding the state of

---

[1] G. E. F. Lundell and H. B. Knowles, J. Am. Chem. Soc. *41*, 1801 (1919).

sulfur in the rock, the percentage should be reported in terms of sulfide, in which form the element is most likely to occur. By a procedure that will not be described here, sulfate sulfur can be determined in a separate sample, and then sulfur as sulfide can be found by difference.

2. Since the amount of sulfur present in rocks is so small, the errors due to coprecipitation are not significant in this case.

3. The purpose of the hydrofluoric acid treatment is to remove any silica possibly present in the barium sulfate precipitate.

Vanadium, nickel, cobalt, copper, zinc, and lead.

These constituents, occurring for the most part as traces, may be determined by colorimetric methods.[1]

Statement of analysis.

It has long been customary to report the results of a rock analysis in terms of the oxides (basic oxides and acid radicals) of the elements present.

In a statement of analysis the constituents are logically reported in the following order:[2]

SiO_2, TiO_2, Al_2O_3, Fe_2O_3, FeO, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5, $H_2O +$, $H_2O -$, CO_2, ZrO_2, F, Cl, SO_3, S, $(Ce, Y)_2O_3$, Cr_2O_3, V_2O_3, NiO, CoO, BaO, SrO, BeO, CuO, Li_2O, B_2O_3.

For the sake of uniformity and to facilitate comparison of analyses, this order should always be followed.

If a constituent has not been looked for, a dash should follow that constituent in the tabulation of the results; or the letters *n. d.* may be used to indicate that it has not been determined. If a constituent has been looked for but not found, the fact should be indicated by 0.00 or "none" or "nil." A constituent sought for and found to be present in unweighable amounts (< 0.1 mg.) is reported as a *trace*.

The percentages of the constituents should be reported to two decimal places, in accordance with the rule that the first doubtful figure of a value should be given. Percentages are referred to the air-dry sample.

Summation of results.

Although a summation of results that is very nearly equal to 100 per cent does not necessarily indicate that the analysis is correct, a failure to obtain a satisfactory summation is definite proof of error in the determination of one or more constituents or the omission of one or more constituents, and thus furnishes a valuable check on the accuracy of the work.

Hillebrand[3] sets the limits of a satisfactory summation at 99.75 and 100.50 per cent. Washington[4] more liberally places the limits at 99.50

---

[1] For the determination of vanadium (and minute amounts of chromium and molybdenum), see E. B. Sandell, Ind. Eng. Chem., Anal. Ed. *8*, 336 (1936); for nickel and cobalt, E. B. Sandell and R. W. Perlich, *ibid. 11*, 309 (1939); for copper, zinc, and lead, E. B. Sandell, *ibid. 9*, 464 (1937).

[2] H. S. Washington, *The Chemical Analysis of Rocks*, 4th ed., p. 23.

[3] W. F. Hillebrand, *The Analysis of Silicate and Carbonate Rocks*, p. 30.

[4] H. S. Washington, *ibid.*, p. 144.

and 100.75 per cent. The student who runs a rock analysis for the first time, probably with a limited amount of platinum ware, may well be content with a summation falling within Washington's limits.

If all the constituents present have been determined, the tendency is to obtain a summation greater than 100 per cent. This tendency is to be attributed to the presence of small amounts of the common constituents in the reagents employed, the attack of the vessels used, and the presence of small amounts of foreign substances (water, for one) in the precipitates or residues weighed.

It should be noted that a summation involving acid radicals not reported as oxides (F, Cl, S) should be corrected by deducting the oxygen equivalent of these.

APPENDIX

APPENDIX

TABLE LXXII. DENSITY OF WATER[1]

(Under standard pressure of 760 mm. of mercury)

TEMPERATURE ° C.	DENSITY G./ML.	TEMPERATURE ° C.	DENSITY G./ML.
15	0.99913	26	0.99682
16	0.99897	27	0.99655
17	0.99880	28	0.99627
18	0.99862	29	0.99598
19	0.99843	30	0.99568
20	0.99823	31	0.99537
21	0.99802	32	0.99506
22	0.99780	33	0.99473
23	0.99757	34	0.99440
24	0.99733	35	0.99406
25	0.99708		

[1] P. Chappuis, *Travaux et mémoires du Bureau International des Poids et Mesures*, Vol. XIII (1907).

TABLE LXXIII. APPROXIMATE DENSITIES AND MOLARITIES OF CONCENTRATED ACIDS AND AMMONIA

	PER CENT BY WEIGHT	DENSITY	MOLARITY
Acetic acid	99.5	1.05	17.4
Ammonium hydroxide	27 (NH_3)	0.90	14.3
Hydrochloric acid	37	1.18	12.0
Hydrofluoric acid	48	1.15	27.6
Nitric acid	70	1.41	15.7
Perchloric acid	70	1.66	11.6
Phosphoric acid	85	1.69	14.7
Sulfuric acid	95.5	1.83	17.8

Table LXXIV. Densities of Acids and Ammonia at 20° C.

Weight Per Cent	Density					
	CH_3COOH	HCl	HNO_3	H_3PO_4	H_2SO_4	NH_3
5	1.0055	1.023	1.026	1.025	1.032	0.977
10	1.0125	1.047	1.054	1.053	1.066	0.958
15	1.0195	1.073	1.084	1.082	1.102	0.940
20	1.026	1.098	1.115	1.113	1.139	0.923
25	1.033	1.124	1.147	1.146	1.178	0.907
30	1.038	1.149	1.180	1.181	1.219	0.892
35	1.044	1.174	1.214	1.216	1.260	
40	1.049	1.198	1.246	1.254	1.303	
45	1.053		1.278	1.293	1.348	
50	1.058		1.310	1.335	1.395	
55	1.061		1.339	1.379	1.445	
60	1.064		1.367	1.426	1.498	
65	1.067		1.391	1.475	1.553	
70	1.069		1.413	1.526	1.611	
75	1.070		1.434	1.579	1.669	
80	1.070		1.452	1.633	1.727	
85	1.069		1.469	1.689	1.779	
90	1.066		1.483	1.746	1.814	
95	1.061		1.493	1.807	1.834	
100	1.050		1.513	1.870	1.831	

INDEX OF AUTHORS

A

Aas, F., 684
Adams, L. H., 332, 335, 337
Agruss, M. S., 373
Aitcheson, L., 704
Akiyama, T., 71
Allen, A. H., 9
Allen, E. T., 8, 179, 335, 337, 343
Allen, W. S., 343
Allmand, A. J., 152
Allsopp, C. B., 656
Almy, E. G., 305
Andrews, L. W., 585, 595
Andrussow, L., 352
Archibald, E. H., 161
Arenson, S. B., 16
Arnd, Th., 564
Arnold, F. W., 82
Arny, H. V., 654
Arrhenius, O. S., 678
Ashby, E. C., 305
Ashley, S. E. Q., 652
Atack, F. W., 77
Austin, M., 365
Axelrod, M., 679
Axilrod, H. D., 410

B

Bachmann, W., 108
Balanescu, G., 81
Balarew, D., 365
Ball, E. G., 629
Ball, T. R., 373
Baly, E. C. C., 692
Barber, H. H., 416, 417
Barker, H. H., 687
Barker, T. V., 165
Barneby, O. L., 747
Barnitt, J. B., 191
Bassett, H., 6, 605
Baudisch, O., 76
Bauer, O., 730
Baxter, G. P., 219, 307, 308, 318, 414, 593
Beamish, F. E., 78
Bechhold, H., 690
Becker, E., 80
Beckurts, H., 7
Beekley, J. S., 115
Beer, 647
Bell, W. R. P., 305
Bemmelen, J. M. van, 134
Bendix, G. H., 78
Benedetti-Pichler, A. A., 8, 269, 277, 280, 281
Bent, H. E., 671
Berg, R., 78, 79, 80, 85, 327, 373, 587
Berger, H. W., 179
Bergman, T., 29
Berl, E., 9
Bernard, F., 647
Berzelius, J. J., 262, 752
Billheimer, J. J., 405
Biltz, H., 7, 184
Biltz, W., 7, 184
Bingham, E. G., 686
Birnbaum, N., 392
Bishop, H. B., 343
Bjerrum, N., 8
Blade, E., 223, 228
Blair, A. A., 730
Bliss, H. H., 586
Blum, W., 324, 325, 326, 709
Blumenthal, H., 98
Bobtelsky, J., 357
Boldyreff, A. W., 353
Bömer, A., 9
Bonner, W. D., 545
Booth, H. S., 191
Bormann, K., 678
Bornstein, 683
Bose, M. K., 84
Bothe, W., 687
Böttger, W., 7, 156, 680
Bower, J. H., 191
Bowles, J. A. C., 69
Bradley, W. M., 353
Brantner, H., 83
Brawley, D. J., 699
Bray, W. C., 500, 596, 624
Brennecke, E., 7
Bridges, R. W., 704
Bright, H. A., 373, 594, 707, 711, 731
Brinton, P. H. M-P., 213, 412
Britton, H. T. S., 69, 509, 684

Brode, W., 664
Brönsted, J. N., 680
Brown, C. T., 678
Browne, C. A., 9, 686
Brukl, A., 85
Brunck, O., 77, 187, 350, 400, 722
Brush, G. J., 753
Bryant, W. M. D., 305
Bube, K., 365, 369
Bucherer, H. T., 403
Bunsen, R., 647
Burford, M. G., 88
Burgess, G. K., 178, 179
Burgstaller, A., 477
Busch, M., 81

C

Cake, W. E., 404
Caldwell, J. R., 109, 477, 573
Caley, E. R., 88, 410, 416, 678
Carr, R. H., 9
Chamot, E. M., 8, 693
Chan, F. L., 347
Chandelle, R., 83
Chandlee, G. C., 82, 83
Channon, H. J., 688
Chapin, R. M., 622
Chapman, H. D., 350
Chapman, R. P., 494
Chappuis, P., 764
Chatelet, L., 678
Chirnside, R. T., 80, 373, 374
Cholnoky, L., 91
Churchill, H. V., 704
Cittert, M. J. van, 331
Clabaugh, W. S., 175. 176
Clark, W. M., 492
Clarke, B. L., 160
Clarke, F. W., 376, 734
Classen, A., 7, 8, 420
Clay, J. P., 112
Clennell, J. E., 704
Cloeren, H., 8
Cohnstaedt, 133
Cole, H. I., 60
Coltman, R. W., 709
Contat, A., 589
Cox, H. E., 9
Craig, A., 201
Craig, K. A., 82
Crane, E. J., 6, 10
Crismer, L., 687
Crockford, H. D., 699
Crowell, W. R., 633
Crumpler, T. B., 271
Cunningham, T. R., 709
Curtis, J. A., 76

D

Dammerell, V. R., 679
Dankworth, P. W., 693
Danneel, H., 8, 420
Daudt, H. W., 319
Daynes, H. A., 680
Dehn, W. M., 661
Deiss, E., 236, 730
Demorest, D. J., 731
Dencke, H., 81
Dénigès, G., 7, 479
Dennis, L. M., 680
Derksen, J. C., 137
Derr, R. B., 191
Dhar, H., 78
Dick, J., 83, 310, 351
Diehl, H., 77, 752
Dimitrow, P., 365
Dingemans, H. H., 400
Ditt, M., 75
Dittler, E., 754
Dittrich, M., 754
Dodson, K. W., 91
Doerner, H. A., 111
Dole, M., 504
Domke, J., 684
Donaldson, H. C., 629
Doolittle, R. E., 9
Drucker, C., 683
Dundon, M. L., 102
Dunstan, A. E., 686
Duschak, L. H., 335
Dworzak, R., 83

E

Ebert, L., 684
Edgar, G., 477
Edmonds, S. M., 740
Eggertsen, F. T., 105, 111
Ehrenberg, R., 656
Ehret, W. F., 223
Ehrmann, W., 81, 83
Eigenberger, E., 187
Eisenlohr, F., 684
Eitel, W., 654
Ellingham, H. J. T., 152
Elmquist, R., 112

Emich, F., 8
Engelder, C. J., 16
Ephraim, F., 76
Epperson, A. W., 181, 365, 368, 369
Erlenmeyer, H., 92
Evans, O. M., 613

F

Fahrenwald, F. A., 179
Fajans, K., 7, 474
Fales, H. A., 6, 152, 339
Faust, P. H., 405
Feigl, F., 74, 75, 84, 673
Fife, J. G., 160
Finn, A. N., 175, 176
Fischer, A., 8
Fischer, H., 674
Fischer, K., 305
Fischer, W., 105, 356
Fish, F. H., 380
Fisher, R. A., 276
Flagg, J. F., 76
Fleck, H. R., 80, 373
Fleischmann, O., 404
Fogg, H. C., 82
Foote, H. W., 353
Forbes, G. S., 60
Forney, G. J., 91
Foulk, C. W., 416, 545
Fowler, R. H., 594
Fowler, R. M., 721
French, C. L., 671
Frere, F. J., 81
Frers, J. N., 324, 325
Fresenius, C. R., 7
Fresenius, H., 412
Fresenius, R., 412
Fresnel, 616
Freundlich, H., 102, 686
Friedenthal, H., 678
Friedrich, A., 8
Funk, H., 75
Furman, N. H., 6, 76, 102, 320, 426, 503, 609, 610, 613, 698
Fyleman, E., 8

G

Gallego, M., 81
Garrett, O. F., 417
Gay-Lussac, 470
Geilmann, W., 80
Geist, H. H., 82
Gerber, A. B., 461
Gerdien, H., 181
Gerlach, W., 692
Getz, C. A., 583
Gibbs, W., 365
Gill, A. H., 642
Ginsberg, L. B., 160
Gleu, K., 612
Göckel, H., 589
Goldberg, E., 659
Goldschmidt, H., 684
Gooch, F. A., 7, 185, 365
Gortner, R. A., 102
Goto, H., 80
Goy, S., 350
Gramont, A. de, 691
Grant, J., 693
Greathouse, L. H., 713
Greene, H. S., 678
Gregory, E., 704
Gribnau, F. B., 690
Griffin, R. C., 9, 10
Griffin, W. C., 305
Griffith, F. S., 64, 114
Groschuff, E., 401
Groves, A. W., 733, 745
Guillaume, C. E., 524
Guldberg, C. M., 32
Gupta, J., 84
Gurevich, L. J., 179
Gutbier, A., 81

H

Haase, L. W., 79
Haber, F., 101
Hagen, G., 337
Hahn, F. L., 331, 370, 624
Hahn, F. V. von, 691
Halberstadt, S., 81
Hale, C. H., 718
Hall, D., 83
Hall, N. F., 163
Hall, R. W., 179
Hall, W. T., 7, 730
Halversen, R. A., 123
Hamburger, H. J., 670
Hamilton, L. F., 16
Hammarsten, G., 56, 97
Hammett, L. P., 494, 740
Hammond, W. A., 191
Hantzsch, A., 650
Hanus, J., 77
Hardt, H. B., 370
Harley, J. H. A., 187, 678
Hartley, W. N., 691

Hartwig-Bendig, M., 754
Harwood, H. F., 71, 381
Hassel, O., 474
Hatschek, E., 686
Hawthorne, C. R., 112
Hayman, D. F., 223
Hebler, F., 690
Hecht, F., 81, 83
Heczko, T., 80
Hehner, O., 656
Hempel, W., 240
Henle, F., 305
Henriquez, P. C., 684
Herz, W., 7
Heuber, H., 752
Hevesy, G. von, 693
Hey, M. H., 748
Heyrovsky, J., 513, 517
Hibbard, P. L., 690
Hibbert, E., 8
Hicks, W. B., 413
Hillebrand, W. F., 7, 76, 90, 137, 142, 176, 179, 238, 240, 310, 358, 377, 379, 385, 391, 402, 403, 733, 758, 760
Hills, F. G., 10
Hilton, F. A., 307, 308
Hintz, E., 337
Hitchen, C. S., 692
Hoffman, J. I., 7, 308, 350, 365, 369, 370, 393, 395, 707, 731, 751
Holborn, L., 684
Hollingsworth, M., 545
Holt, E. V., 381
Holtje, R., 400
Holzer, H., 76, 77, 412
Hoover, C. R., 318
Hoskins, W. H., 111
Hostetter, J. C., 318
Hulett, G. A., 102, 179, 335, 545
Hume, D. N., 495, 598
Hummel, F. F., 411
Hurley, F. H., 294, 549
Hüttig, G. F., 187, 188, 189, 308

I

Ibbotson, F., 704, 730
Ihmori, T., 133
Ismail, A. M., 71

J

Jacob, K. D., 370
Jacobs, M. B., 9
Jahr, K. F., 8, 112
James, C., 82
Jamieson, G. S., 8, 585
Jander, G., 8, 108, 112, 509
Järvinen, K. K., 365
Jélek, A., 77
Jilek, A., 81
Johannsen, A., 693
Johnson, C. M., 730
Johnson, C. R., 470
Johnson, F. M. G., 191
Johnston, J., 332, 335, 337, 343
Jolles, A., 672
Jones, C., 598
Jörgensen, G., 365
Juckenack, A., 9

K

Käding, H., 167
Kallmann, S., 98
Kameda, T., 69
Karaoglanow, Z., 112, 329, 365
Karns, G. M., 629
Karsten, P., 646, 654, 671
Kasline, C. T., 650, 654
Kassler, J., 731
Katz, J. R., 137
Kayser, H., 693
Keitt, T. E., 413
Keane, C. A., 9
Kendall, J., 60
Kenny, F., 150
Kerlinger, H., 71
Kiehl, S. J., 370
Kiess, C. C., 692
Kinder, H., 731
Kjeldahl, J., 565
Klobbie, E. A., 134
Knapper, J. S., 82
Knecht, E., 8
Knop, J., 492, 495
Knorre, G. von, 82
Knowles, H. B., 76, 80, 320, 327, 599 727, 739, 759
Kobayashi, M., 414
Koch, P., 325, 404
Kohl, H., 181
Kohlrausch, F., 684
Kolthoff, I. M., 8, 36, 56, 63, 64, 69, 71, 78, 80, 103, 105, 110, 111, 112, 113, 114, 117, 118, 119, 121, 123, 124, 134, 320, 327, 331, 349, 351, 416, 417, 449, 450, 474, 475, 492, 493, 494, 495, 499, 509, 513, 514, 516, 518, 552, 569, 589, 595, 610, 639, 680, 701 711, 725

Konen, H., 693
Koppeschaar, W. F., 587
Kratzert, J., 325, 404
Krauch, G., 163
Krauss, A., 107
Krauss, F., 81
Kraut, H., 401
Kreider, L. C., 201
Krogh, A., 693
Kunzmann, T., 655
Kuras, M., 79
Küstenmacher, H., 79
Kuzirian, S. B., 300

L

Lacey, W. N., 684
Laitinen, H. A., 36, 503, 509, 514, 518, 595
Lambert, 646
Lambie, D. A., 338
Landolt, H., 683, 686
Lang, R., 7, 80, 585, 595
Lange, L. T., 583
Langer, A., 516
Larabee, C. P., 711
Lauer, W. M., 475
Leach, A. E., 9
Le Blanc, M., 150
Ledebur, A., 731
Lenher, V., 401, 402
Lewis, J., 693
Lewkowitsch, J., 9
Liebig, J. von, 479
Liggett, L. M., 752
Lind, S. C., 687
Linder, S. E., 96
Lindsay, G. A., 655
Lingane, J J., 71, 513, 517, 569, 595, 610, 711
Livingston, R. S., 499, 680
Lobinger, K., 401
Lockermann, G., 655
Lockyer, N., 691
Logemann, A., 659
Lord, N. W., 731
Lottermoser, A., 115
Low, A. H., 9
Löwe, Fritz, 684
Lukas, J., 77
Luke, C. L., 160
Lukens, H. S., 156
Lunde, G., 694
Lundegårdh, H., 692
Lundell, G. E. F., 7, 76, 80, 90, 176 238, 239, 240, 308, 310, 320, 327, 350, 365, 369, 370, 377, 379, 385, 391, 393, 395, 403, 599, 707, 709, 731, 733, 739, 751, 758, 759
Lunge, G., 9, 603
Lurie, J. J., 160
Luther, R., 645

M

MacDougall, F. H., 145
Mack, E., 102
MacKenzie, A. A., 596
Magnanini, G., 670
Mahin, E. G., 9
Majer, V., 517
Mäkinen, E., 751
Malkowa-Janowski, Frau, 357
Margosches, B. M., 7
Margueritte, F., 581
Marian, S., 25
Marjanović, V., 332
Mark, H., 693
Mason, C. W., 8, 693
Mauzelius, R., 240
Maxwell-Garnett, J. C., 680
Maxymowicz, W., 72, 187, 188, 189
Mayr, C., 81
McBride, R. S., 593
McCroskey, C. R., 624
McCutcheon, T. P., 142, 156
McIntyre, L. H., 191
McLennan, I. C., 373, 374
Meade, R. K., 704
Mears, B., 421
Meene, G. H. P. van der, 701
Meggers, W. F., 692
Mehlig, J. P., 654
Meier, F. W., 403, 404
Mellan, I., 74
Mellon, M. G., 6, 10, 650, 654, 670, 673
Mellor, J. W., 7, 123, 276
Menzel, E., 308, 549
Merck, E., 163
Merrill, H. V., 401
Merritt, L. J., 497
Merwin, H. E., 744
Merz, J. A., 81
Meusser, 176
Michaelis, L., 492
Michailowa, N. F., 109
Middleton, E. B., 97

Mie, G., 690
Miehr, W., 325
Miles, F. T., 461
Miller, C. C., 373, 374, 417
Miller, E. H., 16
Miller, H. E. 624
Mitchell, A. D., 7
Mitchell, J., 305
Mohr, Fr., 470
Moltzau, R., 114
Montequi, R., 81
Moore, R. B., 10
Moser, L., 25, 72, 85, 172, 187, 188, 189, 351
Moskovitz, B., 71, 119, 320, 589
Mosttowitsch, W., 339
Moyer H. V., 80, 573
Moyer, M. V., 109
Muehlberg, W. F., 400, 718
Müller, E., 503
Müller, R. H., 652, 680
Mumbrauer, R., 167
Munroe, C. E., 187
Murray, B. L., 163
Mylius, F., 176, 401

N

Naish, W. A., 704
Nessler, J., 668
Neth, W., 188
Neubauer, H., 365
Neuhausser, A., 692
Neuman, E. W., 55, 337
Neurath, F., 672
Nichols, M. L., 668
Niederl, J. B., 9
Niederl, V., 9
Niessner, M., 85
Nieuwenburg, C. J. van, 400
Njegovan, V., 332
Noll, W., 745
Noponen, G., 105, 111

O

O'Brien, A. S., 105
Ohlmüller, W. O., 10
Oknin, I. V., 678
Ordelt, H., 84
Ostraumow, E. A., 71
Ostwald, W., 6, 256
Otto, I. R., 331
Overholser, L., 119, 124
Overman, O. R., 417
Owe, A. W., 690

P

Palkin, S., 410
Pan, Y. D., 516
Paneth, F., 686
Park, B., 632
Parker, H. G., 333, 335, 678
Parks, 133
Partridge, H. M., 69
Patterson, A. M., 6, 10
Pearson, E., 112
Penfield, S. L., 753
Perlich, R. W., 56, 760
Peter, O., 659
Pfundt, O., 509
Phillips, F. C., 731
Picton, H., 96
Pihlblad, N., 690
Pine, P. R., 421
Pirtea, T. I., 80
Pope, T. H., 9
Popoff, S., 55, 337, 624
Popper, R., 678
Powell, A. R., 10, 85
Power, F. W., 276
Prausnitz, P. H., 184, 187
Pregl, F., 9
Prentice, D., 181
Price, H. P., 678
Price, W. B., 704
Pristera, F., 98
Pritchard, C. F., 80, 373, 374
Prodinger, W., 74

R

Radley, J. A., 693
Rae, W. N., 683
Ramsey, J. B., 500
Rankama, K., 405
Rawson, S. G., 745
Ray, P., 78, 84
Ray, R. M., 78
Redmond, J., 80, 373
Reich-Rohrwig, W., 81, 83
Reif, W., 76
Reifer, J., 80
Reilly, J., 683
Reimerdes, E. 684
Reinhart, C., 678
Reith, J. F., 629
Remington, W. R., 80, 81
Remy, H., 410
Renwick, F. F., 688
Reynolds, D. S., 370
Rice, A. C., 82

Richards, T. W., 163, 224, 308, 333, 335, 470, 568
Rideal, E. K., 686
Rieman, W., 337
Ring, C. H., 654
Robinson, R. J., 673
Rodden, C. J., 223
Roebling, W., 85
Roebuck, J. R., 621
Rolfe, G. W., 686
Rooksby, H. P., 80, 373, 374
Roscoe, 647
Roseman, R., 742
Rosenblum, Ch., 105, 117
Rosin, J., 163
Ross, J. F., 414
Roth, W. A., 683, 684
Rothe, A., 115
Rothe, J. W., 90
Rothmund, V., 477
Rowledge, H. P., 748
Rudisüle, A., 7
Rudy, R. B., 181
Russell, J. J., 78
Russell, W. W., 187, 678
Ruthardt, K., 693

S

Sadusk, J. F., 629
Sagortschev, B., 112
Sale, P. D., 178
Sand, H. J. S., 8, 159
Sandell, E. B., 80, 117, 118, 121, 124, 327, 349, 351, 359, 589, 674, 680, 711, 725, 760
Sandera, K., 684
Sarver, L. A., 74, 492, 493, 494, 747
Scheel, K., 683
Scheibe, G., 692
Schleicher, A., 159
Schlesinger, H. I., 670
Schlundt, H., 687
Schmidlin, J., 92
Schmidt, W., 82
Schmitz, B., 363
Schmitz, K., 187, 188
Schoder, W. P., 10
Schoeller, W. R., 10, 85, 338
Schollenberger, C. J., 747
Schoonover, J. C., 610
Schoorl, N., 129, 131, 134, 220, 416, 654
Schwab, G. M., 92
Schwartz, M. C., 672
Schweitzer. E., 692
Scobie, H. F., 731
Scott, W. W., 7, 9, 238, 731
Scripture, Jr., E. W., 191
Seath, J., 78
Seith, W., 693
Shead, A. C., 412, 413
Sherrick, J. L., 122, 338
Shibata, Y., 650
Shiver, H. E., 413
Sibelius, H., 350
Siegbahn, M., 693
Sieger, H., 109
Siegmund, R., 410
Simon, A., 188
Simpson, C. T., 83
Simpson, M. E., 596
Simpson, S. G., 16, 559
Singer, J., 85
Sisco, F. T., 731
Skinner, W. W., 9
Sloan, C. H., 60
Smethurst, A. F., 754
Smith, D. E., 545
Smith, D. M., 305, 692
Smith, E. F., 8, 156
Smith, G. F., 57, 58, 76, 190, 412, 413, 414, 583, 586
Smith, G. M., 85
Smith, J. L., 248, 748
Smith, T. B., 6, 102, 108, 119, 123
Smither, F. W., 176
Snelling, W. O., 187
Sörensen, S. P. L., 164, 549
Sosman, R. B., 318
Soule, B. A., 6, 77, 553
Spacu, G., 79, 83
Spitta, O., 10
Stadeler, A., 731
Stähler, A., 183, 684
Stamm, H., 7
Stas, J., 491
Stein, P. von, 74
Steiner, W., 474
Stenger, V. A., 8, 71, 134, 320, 450, 459, 465, 475, 479, 480, 492, 499, 520, 545, 562, 569, 576, 585, 593, 623, 634, 639
Stevens, R. E., 410, 752
Stevenson, W. W., 704
Stimson, F. J., 692
Stock, A., 183

Stocks, H. B., 163
Stokes, H. N., 376
Stone, H. W., 598
Storr, B. V., 688
Stott, V., 519
Strain, H. A., 92
Straten, C. W. van, 223
Strebinger, R., 412
Strömberg, R., 133
Strutt, J. W., 689
Süe, P., 80, 81
Sunde, C. J., 475
Sutton, F., 8
Swank, H. W., 673
Swett, O. D., 187
Swift, E. H., 91, 405
Swisher, M. C., 411

T

Tang, N. K., 108
Taub, A., 654
Taylor, F. M., 380
Taylor, H. S., 115
Taylor-Austin, E., 80
Teitelbaum, M., 81
Teorell, T., 690
Thiel, A., 659
Thole, F. B., 686
Thomas, A., 112
Thompson, H. V., 7
Thompson, W. S., 339
Thomson, J. J., 690
Thorne, P. C. L., 9
Thornton, Jr., W. M., 10, 742, 744
Tillmans, J., 9
Titus, A. C., 545
Tongeren, W. van, 404, 733, 752
Traves, F., 417
Treadwell, F. P., 7
Treadwell, W. D., 7, 81
Trimble, H. M., 106
Truog, E., 402
Tschugaeff, L., 77
Twyman, F., 664, 692

U

Ukema, M., 678
Ulrich, W., 655

V

Valkenburgh, H. B. van, 670
Vanino, L., 172
Vartanian, R. D., 112
Vicovsky, V., 81
Vierordt, K., 664
Vieweg, K., 373
Villavecchia, V., 9
Vogelenzang, E. H., 63
Volhard, J., 476
Vosburgh, W. C., 624

W

Waage, P., 32
Walden, G. H., 392, 494, 740
Walker, P. H., 176
Walpole, H., 661
Waltenburg, R. G., 178 179
Warburg, E., 133
Ward, A. M., 7, 80, 373
Washburn, E. W., 621
Washington, H. S., 179, 733, 734, 760
Waterhouse, E. F., 85
Waters, C. E., 339
Weatherill, P. F., 229
Webb, H. W., 85
Weber, H., 337
Wedding, H., 678
Weiblen, D., 56
Weigert, F., 664
Weihrich, R., 731
Weimarn, P. P. von, 99
Weinig, A. J., 10
Weiser, H. B., 96, 122, 316, 338
Weisz, L., 109
Wells, H. L., 212
Wells, P. V., 688, 691
Wells, R. C., 308, 410, 470, 568
Wepritzkaja, W., 109
Wétroff, G., 81
Weygand, C., 9
White, A. H., 680
Whitehead, T. H., 112, 496
Whitman, J. L., 624
Wichers, E., 175, 176, 179
Wichmann, H. J., 674
Wilcox, C. S., 305
Wilcox, L. V., 411
Wiley, H. W., 9
Wilkinson, J. A., 16
Willard, H. H., 6, 57, 58, 83, 85, 102, 108, 190, 320, 347, 353, 404, 426, 494, 497, 612, 698, 713, 724, 752
Williams, R. S., 730
Willits, C. O., 668
Willows, R. S., 686
Wills, C. C., 496

Willstätter, R., 401
Winkler, L. W., 290, 339, 350, 369, 655, 672
Winton, A. L., 9
Wirth, H. E., 673
Withrow, J. R., 191
Wolff, H., 474
Wolff, P., 680
Woodman, A. G., 10
Woods, J. T., 671
Wooten, L. A., 160
Wrigge, F. W., 80
Wright, C. H., 10

Y

Yoe, J. H., 74, 271, 652, 659, 688, 691
Young, P., 494, 612, 724
Yutzy, H. C., 105

Z

Zakowski, J., 108
Zanetti, J. E., 593
Zechmeister, L., 91
Zerban, F. W., 9, 686
Zimmermann, K., 319
Zombory, L. von, 351
Zsigmondy, R., 108

INDEX OF SUBJECTS

A

Abrasion, of mortar, 193, 240, 748
Absorbents, for carbon dioxide, 387
  for water, 191
Absorption, coefficient of, 647
  of water, 134
Absorption tubes, in determination of carbon dioxide, 387, 707, 708
  in determination of water, 302
Accidental errors, 270
Accuracy, definition of, 263
  in calculations, 293
  in indirect analysis, 292
  in quantitative analysis, 281
  methods of checking, 284
  methods of increasing, 286
  of a method, 280
Acetate method, 71
Acetic acid, ionization constant of, 37
  neutralization curve of, 456
  specific gravity of, 765
  titration of, 556
Acidimetry, exercises in, 555
  in practice, 545
  theory of, 445
Acid potassium phthalate, 553
Acids,
  densities of, 765
  determination of, conductometrically, 510
    iodometrically, 616
    potentiometrically, 503
  dibasic, 36
  ionization constants of, 37
  neutralization curves of, 451
  polybasic, 459
  standardization of, 546
  strong, 34
  weak, 34, 35
    titration of, 456, 556
  cf. Acidimetry, Alkalimetry
Activity, and solubility, 53, 55
  coefficient, 53
Adapter, for Gooch crucible, 186
Adsorption, 95, 98, 110, 115, 118
  indicators, application of, 571
    theory of, 473
  isotherm, 119, 133
  of moisture, in weighing, 221
Adsorptive properties of precipitates, 115
Aggregation velocity, 101
Aging, and coprecipitation, 123
  of precipitates, 104
Agreement, of results, 284
Air, correction of weights for buoyancy of, 218, 220
  density of, 526
Alcohol, determination of water in, 687
  use of, in drying precipitates, 261
Alizarin yellow, 449
Alkali, bisulfate, use as flux, cf. Pyrosulfate
  hydroxides, as fluxes, 399, 400
    standard solutions of, 550
  pyrosulfate, use as flux, 246, 738
Alkalies,
  determination of, 410
    in silicate rocks, 748
  separation of,
    as chlorides, Berzelius, 752
      Smith, 748
    from calcium, 748
    from magnesium, 748, 751
  standardization of, 553
  standard solutions of, 550
Alkalimetry, application of, 545
  theory of, 445
Allowable differences in determinations, 282, 284
Allowable errors, 283, 284
Alloying elements, in steel, 705
Alumina, as desiccant, 191
Aluminum,
  determination of,
    gravimetric, as hydroxyquinolate, 327
      as oxide, 324
    in silicate rocks, 744
    volumetric, as hydroxyquinolate, 638
  hydrous oxide of, coprecipitation with, 326
    precipitation of, 324
    solubility of, 324

hydroxide, amphoteric properties of, 324
oxide, ignition of, 325
separation of, from beryllium, 327
from iron, 73, 741
from magnesium, 326, 327
from phosphorus, 327
Alundum crucible, 182
Amalgams, use of, in reduction, 498
Ammonia, carbonate-free, 170
determination of, acidimetric, 562
colorimetric, 668
formation of complexes with, 60, 70
ionization constant of, 37
neutralization curve of, 457
titration of, with hypochlorite, 640
Ammonium, cf. Ammonia
Ammonium hydroxide, reagent, 170
density of, 765
cf. Ammonia
Ammonium molybdate, as catalyst, 624
as reagent, 714
Ammonium persulfate, 711
Ammonium phosphomolybdate, contaminants of, 393
precipitation of, 391
Ammonium salts, removal of, 248
Ammonium sulfide-tartrate, precipitation by, 73, 741
Amorphous substances, 101
Ampere, 143
Amperometric titrations, 513
Analysis, accuracy of, 4
errors in, 263 *et seq.*
methods of, colorimetric, 5, 645
gasometric, 6
graphical, 682
gravimetric, 5, 23
indirect, 30
macro, 6
micro, 6
microscopic, 693
nephelometric, 688
physico-chemical, 5, 680
qualitative, 1
spectrographic, 691
spectrophotometric, 645, 662
titrimetric, 5, 431
volumetric, 5, 431
X-ray, 693
preliminary qualitative, 1, 2
preparation of sample for, 239
statement of results of, 16
Analytical weights, calibration of, 224
tolerances of, 206
Andrews titration, 585
Anhydrone, 190
Aniline, ionization constant of, 37
Anode, 140, 421
Anthranilic acid, 75
Antimony, determination of, 586
Apparatus, 174
glass, 174
gold, 180
nickel, 181
platinum, 177
porcelain, 177
silica, 175
silver, 181
volumetric, 519
Apron, laboratory, 236
Argentimetric determinations, application of, 568
end point of, 469
exercises in, 569
theory of, 467
Arsenic,
determination of, as pyroarsenate, 397
as sulfide, 397
cf. Arsenious oxide
Arsenic trisulfide, flocculation of, 96
Arsenious oxide, as standard substance, 594, 622
oxidation potential of, 483
reaction with iodine, 615, 621
reducing properties of, 591
standardization of bromate with, 637
ceric sulfate with, 612
hypochlorite with, 640
iodine with, 625
permanganate with, 594
standard solution of, 622
Arsenite, standard solution,
preparation of, 622
stability of, 591
standardization of, 594, 612, 625, 637
Asbestos, preparation of, for Gooch crucible, 186
Ascarite, composition of, 386
use of, 387, 707

Atomic weights, 13
  international, 14
    table of, *inside back cover*
  rational, explanation of, 220
    table of, *inside back cover*
Auranium, 179
Avogadro's number, 13

B

Back E. M. F., 150
Bakelite ware, 182
Balance, accuracy of, 201
  air-damped, 200
  assay, 200
  care of, 232
  chainomatic, 199
  construction of, 197
  keyboard, 200
  magnetic-damped, 200
  micro, 200
  rules for use of, 232
  sensitivity of, 202
Balance arms, inequality in length of, 214, 216
Barium,
  determination of, as sulfate, 339
    in rocks, 759
Barium carbonate, as precipitant, 71
  solubility product of, 54
Barium chromate, solubility product of, 54
Barium hydroxide, 550
Barium iodate, solubility product of, 54
Barium oxalate, solubility product of, 54
Barium oxide, as desiccant, 191
Barium perchlorate, as desiccant, 191
Barium sulfate, contaminants of, 330
  coprecipitation with, 122, 123
  errors in precipitation of, 333
  filterability of, 94
  ignition of, 339
  size of, in precipitations, 100
  solubility and particle size, 103
  solubility and temperature, 57
  solubility of, 329
    in nitric acid, 63
    in potassium nitrate, 55
  solubility product of, 54
Bases, standardization of, 553
  strong, 34
  weak, 37
Basic acetate method, 71
Beer's Law, 647
  deviations from, 648
Benzidine, 75
Benzoate method, 71
Benzoic acid, for standardization of bases, 554
  ionization constant of, 37
α–Benzoinoxime, 75, 727
Benzotriazole, 76
Beryllium,
  separation of, from aluminum, 327
    from iron, 741
Bibliography, of quantitative analysis, 6
Bicarbonate, titration of, 556
Bismuthate method, for manganese, 709
Blank analyses, 287
Blast lamp, 182
Bleaching powder, 626
Block, Stock-Stähler, 183
Boats, 707
Bolting cloth, 735
Borax, standardization of acids with, 549
  titration of, 560
  water vapor tension of, 130
Borda's method of weighing, 216
Bordeaux, as indicator, 586, 640
Boric acid, ionization constant of, 37
  titration of, 560
Boric oxide, as flux, 752
Bottles, for reagents, 164, 169
  wash-, 191
Brass, analysis of, 697
Bromate, iodometric determination of, 623
  cf. Potassium bromate
Bromcresol green, 449
Bromide,
  determination of, gravimetric, 313
    mercurimetric, 577
    volumetric, Fajans, 475, 571
      Mohr, 471, 570
      Volhard, 478, 573
Bromine, use in precipitation of manganese, 380
Bromphenol blue, 449
Bromthymol blue, 449
Brunck crucible, 187
Buffer, action, 43
  solutions, 44
  solutions and solubility, 70

Burets, 520
  calibration of, 534
  chamber, 542
  rate of flow from, 522, 535, 538
  reading of, 521
  tolerances of, 523
  use of, 538
  weight, 542
Burners, blast, 182
  Meker, 182
  Tirrill, 182

C

Cadmium, determination of, as pyrophosphate, 373
Calcite, for standardizing acids, 550
Calcium,
  determination of,
    gravimetric, as carbonate, 351
      as fluoride, 355
      as oxalate monohydrate, 347, 350, 358
      as oxide, 353
      as sulfate, 339, 354
    in limestone, 382
    in silicate rocks, 744
    volumetric, with permanganate, 605
  precipitation of, as oxalate, 347
  separation of, from alkalies, 348, 349
    from barium, 348
    from magnesium, 355, 359
    from strontium, 348
Calcium carbonate, dissociation pressure of, 351
  solubility product of, 54
  weighing form for calcium, 351
Calcium chloride, as desiccant, 191
Calcium fluoride, weighing form for calcium, 355
  solubility product of, 54
Calcium hypochlorite, as standard solution, 639
  oxidizing properties of, 587
  cf. Bleaching powder
  cf. Hypochlorite
Calcium oxalate, coprecipitation with. 121, 125, 348, 349, 357, 359
  ignition of, 351, 355
  precipitation of, 347
  solubility of, 345
    in sodium chloride, 56
  solubility product of, 54
Calcium oxide, as desiccant, 191
  as weighing form for calcium, 353
Calcium sulfate, as desiccant, 191
  as weighing form for calcium, 354
  solubility product of, 54
Calculation factor, 29
Calculations, accuracy of, 293
  of gravimetric analysis, 28
  of volumetric analysis, 438
Calibration,
  of volumetric glassware, 524
    burets, 534
    flasks, 531
    pipets, 533
  of weights, 224
    by substitution, 225
    by transposition, 229
  table, for volumetric ware, 527
Calomel electrode, 505
Carbon, determination of, in steel, 706
Carbonate,
  titration of, 548
    in presence of bicarbonate, 556
Carbonate rocks, analysis of, 377
  composition of, 376
Carbon dioxide,
  determination of,
    in limestone, 383
    in water, 552
      distilled, 170
  titration of, 558, 559
Carbonic acid, ionization constants of, 37
  neutralization curve for, 461
  titration of, 558, 559
  cf. Carbon dioxide
Casseroles, 177
Catalysts, 33
Catalytic methods, 680
Cathode, 140, 421
Cells, electromotive force of, 147
Centrifuge, 194
Ceric ammonium sulfate, 611
Ceric sulfate, oxidation potential of, 583
  oxidizing properties of, 583
  standard solution of, 611
  titrations with, 613
Cerium, cf. Ceric sulfate
Cesium, determination and separation of, 410
Chamber buret, 542
Chemical factor, 29
Chemicals, purity of, 162

Chloride,
  determination of,
    argentimetric, Fajans, 473, 571
      Mohr, 471, 569
      Volhard, 476, 573
    gravimetric, 307
    mercurimetric, 479, 576
  precipitation curve of, 469
Chlorine,
  determination of, gravimetric, 307
    in bleaching powder, 626
    in rocks, 757
    in soluble chloride, 311
    nephelometric, 308
  cf. Chloride
Chlorophenol red, 449
Chloroplatinic acid, as reagent, 411
Chromatography, 91
Chromic acid, ionization constant of, 37
Chromite, decomposition of, 246
Chromium,
  determination of, colorimetric, 759
    gravimetric, 322
    in silicate rocks, 759
    in steel, 723
    volumetric, 624, 724
Chronometric methods, 685
Cinchonine reagent, for tungsten, 728
Citric acid, ionization constants of, 37
Cleaning, of glassware, 235, 523
  solution, 235, 523
Clear point, 470, 572
Cobalt,
  determination of, electrolytic, 426
    with potassium nitrite, 603
  separation of, with α-nitroso-β-naphthol, 82
Cobaltinitrite method, for cobalt, 603
  for potassium, 411, 603
Colloidal precipitates, 94, 118
Colloidal solutions, 93
  cf. Sols
Color change interval, 447, 448, 449
Colorimeter, 657
Colorimetric apparatus, 652
Colorimetric determination, of ammonia, 668
  of chromium, 759
  of copper, 674
  of iron, 670
  of manganese, in silicate rocks, 755
    in steel, 713
  of silica, 672
  of titanium, in rocks, 742
Colorimetric titrations, 654
Colorimetry, 5, 645
  absolute, 659
  reactions in, 651
  sources of error in, 660
  theory of, 646
Columbium, separation from tantalum, 85
Combined oxides, determination of, in limestone, 380
Combined water, 138
Combining weights, 12
Combustion tube, 706
Common ion effect, 50
Common operations of quantitative analysis, 235
Comparison solutions, 541
  in colorimetry, 654
Complex dissociation constant, 59
Complex formation, analysis by, 478
  and acidimetry, 464
  and colorimetry, 650
  and separations, 72
Complex ions, and solubility, 58
Complex materials, analyses of, 695
Computations, 294
Concentration polarization, 158
Conductivity, electrical, 684
  cf. Conductometric titrations
Conductometric titrations, 509
  cell for, 512
Constant boiling hydrochloric acid, 545
Constant errors, 265
Contamination, of precipitates, 110
  of sample, by agate mortar, 193 240
    by steel mortar, 748
Contat-Göckel trap, 589
Controls, increasing accuracy by, 288
Conversion factor, 29
Copper,
  determination of, electrolytic, 423
      in brass, 701
    photometric, 674
    volumetric, by iodide, 630
      by thiocyanate, 701
      in ores, 632
  dithizonate, 674
  separation of, from nickel, 425
    from zinc, 701
  sulfide, solubility product of, 64
  cf. Cupric copper
Coprecipitation, 110

Corrections, for weights, 231
  in analysis, 287
Coulomb, 143
Counter electromotive force, 149
Counter ions, 95
Cresol purple, 448
Cresol red, 448
Crucibles, alundum, 182
  Brunck, 187
  glass, 188
  Gooch, 185
  iron, 181
  Munroe, 187
  nickel, 181
  palau, 179
  platinum, 178
  porcelain, 177
  porous porcelain, 187
  quartz, 175, 189
  silica, 175, 189
  silver, 181
  Smith, J. Lawrence, 181, 749
Crucible tongs, 194
Crushing, of sample, 192
  in rock analysis, 735
Cryoscopic titration, 501
Crystal hydrates, deliquescence of, 130
  efflorescence of, 130
  vapor pressure of, 128
Crystallization, by change of solvent, 167
  isothermal, 164
Crystals, inclusions in, 137
  size of, 102
Cupferron, 76
Cupric copper, determination of, iodometric, 630
  oxidation potential of, 483
  cf. Copper
Cupron, 75
Cuprous iodide, solubility product of, 54
Cuprous thiocyanate, solubility product of, 54
Current, electric, 140
Cyanide,
  determination of, argentimetric, 478, 574
    mercurimetric, 575

D

Damping, of balance, 200
Data, recording of, 237
Decomposition voltage, 149
Decrepitation, 137
Dehydrating agents, cf. Desiccants
Dehydration, of silica, 402
Deliquescence, 130
Density, definition of, 217
  in analysis, 678, 684
  of air, 526
  of acids, 764, 765
  of ammonia, 764, 765
  of water, 764
Desiccants, 191
Desiccators, 190
  use of, 260
Determinate errors, 265
Deviation, 264, 273
  standard, 271, 273
Diacetyldioxime, 77
Dichlorofluorescein,
  as indicator, application of, 571
    theory of, 474
Dielectric constants, 685
Digestion of precipitates, 122
Di-iodofluorescein, as indicator, 571
Dimensions (units), 93
Dimethylaminoazobenzene, 448
Dimethylglyoxime, 77
  as reagent for nickel in steel, 722
Diphenylamine, 492
Diphenylamine sulfonic acid, 493
Diphenylbenzidine, 492
Diphenyl-endo-anilo hydro-triazole 81
Diphenylthiocarbazone, 674
Dipicrylamine, 78
Direct methods of analysis, 24
Disk, perforated, for Gooch crucible 186
Dissociation, degree of, 34
  electrolytic, 35
  in colorimetry, 649
  thermal, 88
Distillation, separation by, 86
Distilled water, 170
  preparation of, 171
  purity of, 170
  testing of, 170
Distribution, constant, 89
  method, 88
Dithizone, 674
Dolomite, 376
Double layer, 95
Double precipitation, 119
Dry basis, 241

- Drying, of precipitates, 27, 258
  - of sample, 240

E

- Efflorescence, 130
- Electrical apparatus, 183
  - hot plate, 183
  - oven, 183
- Electrical conductivity, cf. Conductivity
- Electrical double layer, 95
- Electrical units, 143
- Electrification, of vessels weighed, 223
- Electroanalysis, theory of, 140, 154
- Electrochemical equivalent, 144
- Electrode potentials, 144
- Electrodes, 140
  - cleaning of, 422
  - platinum, 421
  - tantalum, 421
- Electrolysis, 140
  - apparatus for, 420
  - laws of, 142
- Electrolytes, ion concentration in, 34
  - strong, 34
  - weak, 34
- Electrolytic determination, of copper, 423, 701
  - of lead, 700
  - of nickel, 426
- Electrometric titrations, 502
- Electromotive force, 145
- Electroseparations, 156
- Empirical methods, 434
- Emulsoids, 94
- End point, 431
- Eosin, as adsorption indicator, 475, 571
- Equal turbidity method, 469
- Equilibrium, reversible, 32
- Equilibrium constant, 33
- Equivalence point, 431
- Equivalent, 434
- Equivalent weight, 434
- Erioglaucine A, 495
- Eriogreen B, 495
- Errors, accidental, 270
  - additive, 269
  - constant, 265
  - definition of, 263
  - determinate, 265
  - in colorimetry, 660
  - in derived result, 277
  - indeterminate, 270
  - in quantitative analysis, 262
  - in volumetric analysis, 442
  - methodic, 268
  - operative, 266
  - personal, 267
  - proportional, 269
- Ether, drying of precipitates by, 261
  - extraction of chlorides by, 91
- Evaporation, 247
- Evolution method for sulfur in steel, 719
- Exchange adsorption, 116
- Expression, of results, 16, 17
- External indicator, 432
- Extinction, coefficient, 647
  - exponent, 663
- Extraction, 88
  - of metal chlorides by ether, 91

F

- Factor, calculation, 29
  - chemical, 29
- Factor weights, 244
- Faraday, 144
- Faraday's laws, 142
- Ferric alum, indicator, 475, 573
- Ferric iron,
  - determination of, colorimetric, 670
    - gravimetric, 315
    - in silicate rocks, 741
    - iodometric, 635
  - reduction of, 596
  - separation of, by extraction, 91
  - cf. Iron
- Ferric oxide, determination of, in silicate rocks, 741
  - ignition of, 318
- Ferric oxide, hydrous, adsorption by, 317
  - precipitation of, 316
  - solubility of, 315
  - washing of, 316
- Ferricyanide, determination of, volumetric, 624
  - oxidation potential of, 483
  - cf. Potassium ferricyanide
- Ferrocyanide, determination of, volumetric, 613
  - oxidation potential of, 483
  - standard solution of, 591
  - cf. Potassium ferrocyanide
- Ferrous ammonium sulfate, cf. Mohr' salt

Ferrous iron, determination of, in silicate rocks, 746
  oxidation by grinding, 240, 747
  titration, with ceric sulfate, 486, 611
    dichromate, 608
    permanganate, 595
  cf. Iron
Ferrous materials, analysis of, bibliography, 730
Ferrous salts, as reducing agents, 588
Filterability of precipitates, 98, 99
Filter crucibles, cf. Crucibles
Filter paper, 184, 250
  macerated, 185
Filtration, with paper, 250
  with filter crucibles, 257
Flasks,
  volumetric, calibration of, 531
    testing of, 532
    tolerances of, 522
    use of, 535
Flocculation of sols, 95
Flocculation value, 96
Fluid inclusions, 137
Fluidity, 686
Fluorescein,
  as indicator, application of, 571
    theory of, 473
Fluoride,
  complex formation, with Ce^{IV}, 485, 611
    with Fe^{III}, 484, 615, 631
Fluxes, 246
Formation of precipitates, 93
Formic acid, ionization constant of, 37
Funnels, Büchner, 189
  ordinary, 184
α-Furil dioxime, 77
Furnace, electric, 183
Fusions, sodium carbonate, 399, 406
  potassium pyrosulfate, 738

G

Gallium, separation from various metals, 85
Gas analysis, 679
Gases, 172
Gasometric methods, 6, 679
Gauss' method of weighing, 215
Gauze, wire, 193
Glassware, analytical, 174
  volumetric, 519
Gold, apparatus of, 180
Gooch crucible, 185
Gram, 205
Gram-equivalent, 434
Gravimetric analysis, methods of, 23
Grease, stopcock, 190
Grinding, of sample, 239
  change of composition by, 240

H

Hafnium, in rocks, 758
Hehner cylinders, 656
Hexanitrodiphenylamine, 78
Hot plate, 183
Humidity, relative, 129
Hydrazine, ionization constant of, 37
Hydrazine sulfate, for standardizing alkalies, 555
Hydrochloric acid, constant boiling, 545
  density of, 764, 765
  standardization of, 546
  standard solution of, 545
  cf. Chloride
Hydrofluoric acid,
  density of, 765
  ionization constant of, 37
  method for iron, 746
Hydrogen, for reduction, 597
  non-essential, 136
  overvoltage of, 153
Hydrogen cyanide, ionization constant of, 37
  cf. Cyanide
Hydrogen electrode, 503
  normal, 145
Hydrogen ion concentration, 35
  and solubility, 61, 70
  in buffer solutions, 43
  in hydrolyzed salts, 41
  in mixtures of weak acids and salts, 43
  in mixtures of weak bases and salts, 44
  in strong acids, 35
  in water, 38
  in weak acids, 35
  in weak bases, 36
  cf. Hydrogen ion exponent
Hydrogen ion exponent, 39
  cf. Hydrogen ion concentration
  cf. pH
Hydrogen peroxide,
  determination of, iodometric, 630
    permanganimetric, 604

Hydrogen peroxide — *Continued*
  reaction of, with hypochlorite, 588
  use, as oxidizing agent, 497
    reagent for titanium, 742
Hydrogen sulfide, determination of, iodometric, 634
  ionization constants of, 37
  precipitation with, 63
  reduction with, 597
Hydrolysis, of salt solutions, 40
Hydrolysis constant, 42
Hydrolytic precipitation, 72, 464
Hydrophobic colloids, 94
Hydrophylic colloids, 94
Hydrorubeanic acid, 78
Hydrous ferric oxide, flocculation of, 97
  cf. Ferric oxide
Hydrous oxides, effect of ammonia on, 70
  orientation velocity of, 101
  precipitation of, 107
    and pH, 70
  separation of, 68
Hydroxylamine, reaction with ferric iron, 596
Hydroxyl ion concentration, in strong bases, 35
  in water, 38
  cf. Hydrogen ion concentration
Hydroxyl ion exponent, 39
8-Hydroxyquinolates, table of, 80
8-Hydroxyquinoline, 78
  volumetric application of, 638
Hygroscopic water, 118, 134
  determination of, 240, 299
    in silicate rocks, 753
  cf. Water
Hygroscopicity, 128
Hygrostats, 131
Hypobromite, as oxidizing agent, 587, 640
Hypochlorite, as oxidizing agent, 587, 639
  determination of, iodimetric, 627
  cf. Bleaching powder

I

Igneous rocks, analysis of, 733
  composition of, 734
Ignition, loss on, determination of water by, 25, 299, 755
  of precipitates, 27, 258, 261
Imbibition, 134, 137
Indicators, 431
  acid-base, 445
  adsorption, 473
  mixed, 450
  oxidation-reduction, 491
Indirect methods of analysis, 24, 30, 292
Induced reactions, 434, 498
Internal indicators, 432
Internal surface, 105
International atomic weights, *folde in pocket*
Invert sugar, use of, in titration o boric acid, 560
Iodide, air oxidation of solution, 617
  determination of,
    argentimetric, Fajans, 475, 572
      Mohr, 472, 570
      Volhard, 476, 573
    gravimetric, 313
    in presence of chloride, 572
    iodimetric, 628, 629
    potentiometric, 508
  oxidation potential of, 483
  oxidation with chlorine (bromine) 628
  oxidation with nitrite, 629
  precipitation curve of, 469
Iodimetry, 614
  exercises in, 626
  sources of error in, 617
Iodine, distribution coefficient of, 8
  oxidation potential of, 483
  oxidizing properties of, 584
  reaction of, with arsenious oxid 621
    with thiosulfate, 619
  sensitivity of, with starch, 618
  standard solution of, 622
  titration of, 625
  volatility of, from solution, 618
Iodine monochloride, as catalys 612
Iodometry, cf. Iodimetry
Ion concentration, 34
  in electrolyte solutions, 35
Ionic balance, 285
Ionization constant, of acids, 35
  of bases, 36
Ionization product of water, 38
Iron,
  determination of, colorimetric,
    gravimetric, 315
    in brass, 702

    in ferrous ammonium sulfate, 320
    in ores, 600, 609
    in rocks, 741, 746
    volumetric, 595, 608
  oxidizability of ferrous, 588
  reduction of, 596
  separation of, from other metals, 320
  cf. Ferric and Ferrous
Iron ores, composition of, 600
  determination of iron in, 600, 609
Iron oxide, ignition of, 318
Isotopes, 14

J

J. Lawrence Smith method for alkalies, 748
Jones reductor, 597
Journals, of analytical chemistry, 10

K

Kilogram, 205
Kjeldahl determination, 565
Koppeschaar titration, 587

L

Labeling, 537
Laboratory notebook, 237
Lambert's Laws, 646
Lanthanum oxalate, coprecipitation with, 112
Law, of electrolysis, 142
  of mass action, 32
  of Ohm, 143
Lead,
  determination of, as chromate, 624
    as dioxide, electrolytically, in brass, 700
      with arsenious acid, 604
    as sulfate, in brass, 699
Lead hydroxide, ionization constant of, 37
Lead oxide, for decomposing silicates, 752
Lead peroxide,
  determination of, iodimetric, 630
    with arsenious trioxide, 604
    with ferrous sulfate, 604
    with oxalic acid, 604
Lead sulfate, solubility of, 58, 699
  weighing form for lead, 339 699
Lead sulfide, solubility product of, 64

Limestone, analysis of, 377
  composition of, 376
  decomposition of, 378, 382
Liter, definition of, 524
Lithium, determination and separation of, 410, 415
Lithium chloroplatinate, as reagent for potassium, 412
Loss on ignition, of limestone, 377, 379

M

Macro methods, 6
Magnesia mixture, 395
Magnesium,
  determination of,
    gravimetric, as 8-hydroxyquinolate, 373
      as $MgNH_4PO_4 \cdot 6H_2O$, 369
      as pyrophosphate, 362, 371
    in limestone, 382
    in silicate rocks, 745
    volumetric, as hydroxyquinolate 638
  errors in determination of, 365, 369
  separation of, from alkalies, 374
    from calcium, 355, 359, 371
Magnesium ammonium phosphate, coprecipitation with, 365
  ignition of, 369
  precipitation of, 362, 365, 372, 392, 395
  solubility of, 362
  washing of, 365
Magnesium carbonate, solubility product of, 54
Magnesium fluoride, solubility product of, 54
Magnesium hydroxide, solubility product of, 54
Magnesium hydroxyquinolate, 373
Magnesium oxalate, occlusion of, by calcium oxalate, 357, 359
  post-precipitation of, 356
  solubility of, 356
  solubility product of, 54
Magnesium perchlorate, as desiccant, 190
Magnesium pyrophosphate, ignition of, 369
Magnifying glass, 194
Manganese,
  determination of, colorimetric, 713, 755

Manganese — *Continued*
  determination of — *Continued*
    gravimetric, as oxide, 322
      as pyrophosphate, 373
    in rocks, 755
    in steel, 709, 710, 713
    volumetric, with bismuthate, 709
      with persulfate, 711
  precipitation of, as hydrous dioxide, 380
Mannitol, use of in titration of boric acid, 560
Mass, definition of, 195
Mass action, 32
  law of, 32
Meker burner, 182
Mercaptobenzthiazole, 79
Mercuric chloride, as reagent, 600
Mercuric nitrate, standard solution of, 575
Mercuric oxide, as precipitant, 71
  for standardizing acids, 550
Mercurimetry, application of, 575
  theory of, 479
Mercurous bromide, solubility product of, 54
Mercurous chloride, solubility product of, 54
Mercurous sulfide, solubility product of, 64
Mercury,
  determination of, gravimetric, as mercurous chloride, 313
    volumetric, 575
Mercury cathode, 156
Metal oxides in precipitations, 71
Metals, normal potentials of, 146
Metal sulfides, solubility products of, 64
Methods, catalytic, 680
  physico-chemical, 5, 680
Methylamine, ionization constant of, 37
Methyl orange, 448, 449, 450
  as acid-base indicator, 448
  as indicator for bromate, 586, 638
  and indigo carmine, 450
Methyl red, 448, 449
Methyl yellow, 448, 449
Micro methods, 6
Microscope, 194
Microscopic analysis, 693
Milliliter, 524
Miscibility, 687
Mixed crystals, formation of, 111
  in purification of solids, 165
"Mixed oxides," determination o
    in limestone, 380
  in silicate rocks, 737
Mixtures, physico-chemical analysi
    of, 681
Mohr's salt, as standard substanc
    595
Mohr titration, application of, 570
  theory of, 471
Moisture, cf. Water
Molar extinction coefficient, 648
Molarity, 32
Mole, 13
Molybdate, as catalyst, 624
  as reagent, 391
Molybdenum, determination wit
    α-benzoinoxime, in steel, 727
Mortar, agate, 192, 193
  mullite, 193
  Plattner, 192, 193
  steel, 192, 193
Muffle furnace, 183
Munroe crucible, 187

N

Nephelometer, 688
Nephelometric methods, 688
Nephelometry, 5, 688
Nernst equation, 144
Nessler tubes, 653
Neutralization curves, of strong acid
    and bases, 451
  of weak acids, 456
  of weak bases, 458
Neutral red, 448
Nichrome triangles, 194
Nickel,
  determination of, argentimetri
      574
    electrolytic, 427
    gravimetric, with dimethyl-gly
        oxime, in steel, 722
    volumetric, with cyanide, 574
  separation of, from copper, 425
Nitrate,
  determination of, acidimetric, 56
    with ferrous sulfate, 589
Nitric acid, density of, 764, 765
Nitrite,
  determination of, with hypochlo
      rite, 587
    with permanganate, 602

Nitrogen, 562, 565
  determination of, by reduction to ammonia, 564
    in organic material, 565
    Kjeldahl, 565
  cf. Ammonia, Ammonium, Nitrate, Nitrite
Nitron, 81
α-Nitroso-β-naphthol, 82
Nitrosophenyl hydroxylamine, 76
Normal hydrogen electrode, 145
Normality, 438
Normal potential, 145
  of metals, 146
Normal solutions, 438
Notebook, laboratory, 237
Nuclei, 104

O

Occlusion, 111, 120
  rules of, 121
Ohm's law, 143
Operations, technique of common, 235
Organic bases, in precipitations, 71
Organic matter, destruction of, 599, 601
Organic precipitants, 74
Organic solvents, for detection of iodimetric end point, 619
Orientation velocity, 101
Osmium tetroxide, as catalyst, 612
Osmotic properties, 687
Oven, for drying, 183
Overvoltage, 152
Oxalic acid, ionization constant of, 37
  reducing properties of, 591
  standardizing alkali with, 554
    permanganate with, 592
Oxidation, definition, 140
Oxidation potential, 147, 482
  at equivalence point, 487
  table of, 483
Oxidation-reduction, indicators, 491, 496
  reactions, 482
Oxidizing agents, 581
Oxine, 78
  cf. 8-Hydroxyquinoline
Oxygen potential, 148

P

Palau, 179
Palladium, determination of, 77
Paper filters, 184
Parallax, errors of, 519
Particle size of precipitates, 99
Partition, cf. Distribution
Penfield method for water, 753
Peptization, 97
Perchloric acid, density of, 764, 765
Perfection of precipitates, 105
Periodate method for manganese, 713
Permanganate, 592
  cf. Potassium permanganate
Peroxide, determination of, iodometric, 630
  cf. Hydrogen peroxide
Persulfate, method for manganese, 710
  oxidations with, 497
pH, 39
  adjustment in precipitation, 45
  adjustment in titrations, 46
  and solubility, 61, 70
Phenanthroline-ferrous ion, 494
Phenol, determination of, bromometric, 586
Phenolphthalein, 448, 449, 450
  and methylene green, 451
Phenol red, 448
Phenylarsonic acid, 82
Phenylhydrazine, 71
Phenylthiohydantoic acid, 83
Phosphate,
  determination of, acidimetric, 561
    colorimetric, 672
    gravimetric, 390
    in rocks, 755
Phosphate rock, determination of phosphorus pentoxide in, 395
Phosphoric acid, ionization constant of, 37
  density of, 764, 765
  neutralization of, 459
  titration of, acidimetric, 561
  cf. Phosphate
Phosphorus,
  determination of,
    gravimetric, as ammonium phosphomolybdate, 396
      as magnesium pyrophosphate, 390
      phosphomolybdic oxide, 397
    in phosphate rock, 395
    in rocks, 755
    in steel, 713
    volumetric by alkalimetric method, 716

Phosphorus — *Continued*
  separation of, from other elements, 390, 391
  cf. Phosphate
Phosphorus pentoxide, as desiccant, 190
Photoelectric spectrophotometer, 665
Physico-chemical methods, 643, 680
  in volumetric analysis, 501
Picrolonic acid, 83
Pipets, 520
  calibration of, 533
  Stas, 520
  tolerances for, 523
  use of, 537
Platino, 179
Platinum, separation from palladium, 82
  substitutes, 179
  ware,
    attack of, 179
      by ferric chloride, 180
      by pyrosulfate, 180, 744
      by sodium carbonate, 180
    care and use of, rules for, 179
    cleaning of, 180
    loss in weight of, on ignition, 178, 261
    permeability to gases, 179
pOH, 39
  cf. pH
Polarimetry, 685
Polarization, 158
Polarographic methods, 685
Policeman, 193, 255
Porcelain ware, 177
Postprecipitation, 113
Potassium,
  determination of, as chloroplatinate, 411
    as cobaltinitrite, 411
    as perchlorate, 414
    as sulfate, 410
    indirect, 418
    in silicate rocks, 748
    volumetric, 603
  separation of, from sodium, 411, 414
Potassium bicarbonate, for standardizing acids, 550
Potassium bi-iodate, for standardizing alkalies, 554
Potassium biphthalate, for standardizing alkalies 553
Potassium bitartrate, for standardizing acids, 550
  for standardizing alkalies, 554
Potassium bromate, as standard substance, 623
  for bromine substitutions, 586
  oxidizing properties of, 585
  standardization of arsenious oxide with, 637
    thiosulfate with, 623
  titration with, 637, 638
Potassium chloroplatinate, 411
Potassium dichromate, oxidation potential of, 483
  oxidizing properties of, 584
  standardization of thiosulfate with, 624
  standard solution of, 608
  titrations with, 608
Potassium ferricyanide, as standard substance, 624
  standardization of thiosulfate with, 624
  cf. Ferricyanide
Potassium ferrocyanide, as standard substance, 578, 591
  reducing properties of, 591
  stability of solution, 591
  cf. Ferrocyanide
Potassium fluotitanate, as standard, 742
Potassium hydroxide, as desiccant, 191
Potassium iodate,
  for standardization of acids, 550
    thiosulfate, 623
  oxidizing properties of, 585
  titrations in hydrochloric acid medium, 585
Potassium perchlorate, 414
  solubility in organic solvents, 58
Potassium permanganate, oxidation potential of, 483
  oxidizing properties of, 581
  stability of solution of, 582
  standard solution of, 592
  standardization of, 592
  standardization of thiosulfate with 625
Potassium pyrosulfate, as flux, 24
  738
Potassium thiocyanate, for standardizing silver, 572
  preparation of pure, 569

Potassium titanium oxalate, as standard, 742
Potentials, cf. Electrode
  cf. Normal
Potentiometer, 507
Potentiometric apparatus, 505
Potentiometric titrations, 502
Precipitates, adsorptive properties of, 114
  aging of, 104
  contamination of, 110
  filterability of, 106
  filtration of, 250, 257
  formation and properties of, 93, 99
  ignition of, 27, 258, 261
  washing of, 252
  cf. Coprecipitation
Precipitation, analysis, volumetric, 467
  by ammonium hydroxide, 70
  by cupferron, 76
  by hydrogen sulfide, 249
  by 8-hydroxyquinoline, 79, 80
  completeness of, 50
  fractional, 65
  technique of, 249
Precipitation forms, 26
Precipitation methods, 23, 26
Precision, definition of, 263
Preparation of sample, 239
  in rock analysis, 734
Primary standard substances, 440
Probability curve, 271
Probability of deviations, 275
Properties, quantitative use of, 680
n-Propylarsonic acid, 82
Protein, determination of, acidimetric, 565
Pycnometer, 194
Pyrex, 174
Pyridine, in precipitations, 71, 83
  ionization constant of, 37
Pyrite, determination of sulfur in, 342
Pyrogallol, 84
Pyrolusite, available oxygen in,
  determination of, iodometric, 605
    with arsenious oxide, 604
    with ferrous sulfate, 604
    with oxalic acid, 604
Pyrosulfate, as flux, 246, 738
  fusion, 738
Pyrrhotite, in rocks, 748

Q

Qualitative analysis, relation to quantitative analysis, 1
Quartering, 735
Quartz ware, 175
Quinaldinic acid, 84

R

Radiator, 184
Radioactive determinations, 687
Rare earths, in silicate rocks, 757
Reaction, acid, 40
  alkaline, 40
  in mixture of weak acid and salt, 43
  in mixture of weak base and salt, 43
  neutral, 40
    cf. Hydrogen ion concentration
Reaction constant, 33
Reagent bottles, 164, 169
Reagents, gases, 172
  liquid, 169
  purification of, 163, 170
  quality of, 162
  solid, 162
  solutions of, 169
Recording of results, 237
Recrystallization, purification of solids by, 163
Reducing agents, 588
Reduction, by amalgams, 498
  by Jones reductor, 597
  definition of, 140
  of ferric salts, 596, 739
  of weighings to vacuo, 218
Refractive index, 681
Refractometric titrations, 502
Rejection of a result, 276
Removal of ammonium salts, 248
Replacement titrations, 462
Reporting of results, 16
Reprecipitation, 119
Resistance glass, 174
Rest point, of balance, 207
Rhotanium, 179
Rider, 198
Rock analysis, silicate, 733
Rothe ether extraction, 90
Rubidium, determination and separation of, 410

S

Salicylaldoxime, 76
Salt bridge, 505

Salt hydrates, vapor pressure of, 128, 132
Salts, hydrolysis of, 40
  solubility of, 49
Sample,
  contamination of, by agate, 193, 240
    by steel, 748
  crushing, in rock analysis, 735
  decomposition of, 245
  drying of, 240
  fusion of, 246
  grinding of, 239
  size of, 278
  weighing of, 241
Sampling, 139, 238
  of metals, 239
  of silicate rocks, 734
Sensitivity, of balance, 202, 209
Separations, 68
  by complex formation, 72
  by electrolysis, 156
  by oxidation or reduction, 73
Significant figures, 293
Silica, contaminants of precipitated, 402, 405
  dehydration of, with hydrochloric acid, 401, 402
    with perchloric acid, 404
  determination of, colorimetric, 672
    gravimetric, 398
    in limestone, 379
    in rocks, silicate, 736
    in silicates, 398, 406, 736
    in water, 673
  hydrofluorization of, 405
  ignition of, 404
  impurities in, 405
  recovery of, unprecipitated, 739
  solubility of, 400
  washing of, 403
Silica cotton, 187
Silica crucibles, 175
Silica gel, as desiccant, 191
Silica triangles, 194
Silicate rocks, analysis of, 733
  composition of, 734
Silicates, decomposition of, 398, 736, 748, 751
Silicic acid, properties of, 401
Silicon, determination of, in steel, 720
Silicon tetrafluoride, 405
Sillimanite, 177
Silver, as reductor, 597, 740
  determination of, gravimetric as chloride, 313
    volumetric, Volhard, 475, 572
      with cyanide, 574
  normal potential of, 146
  preparation of pure, 568
Silver bromate, solubility product of, 54
Silver bromide, solubility in ammonia, 61
  solubility product of, 54
Silver carbonate, solubility product of, 54
Silver chloride, decomposition by light, 309
  drying of, 310
  melting point of, 310
  occlusion by, 308
  precipitation of, 312
  solubility, 49, 307
    and particle size, 103
    and temperature, 57
    in excess of Ag^+ and Cl^-, 50, 51
    in potassium nitrate, 57
    in sodium chloride, 60
    product, 54
  washing of, 308
Silver chromate,
  solubility of, 49
    in excess of Ag^+ and $CrO_4^{=}$, 52
  solubility product of, 54
Silver cyanide, solubility in cyanide, 58
  solubility product of, 54
Silver hydroxide, solubility product of, 54
Silver iodate, solubility product of, 54
Silver iodide, solubility product of, 54
Silver nitrate, preparation of pure, 568
  standardization of, 569
  standard solution of, 568
Silver oxalate, solubility product of, 54
Silver sulfide, solubility product of, 6
Silver thiocyanate, solubility produc of, 54
Silver ware, 181
Soda-lime, 386
Sodium,
  determination of,
    gravimetric, as sulfate, 410
      as uranyl zinc acetate, 416

    indirect, 418
    in silicate rocks, 748
    volumetric, 609
  separation of, from potassium, 415, 416
Sodium bicarbonate, cf. Bicarbonate
Sodium bismuthate, reagent, 709
Sodium carbonate, as flux, 399
  as standard substance, 546
  titration of, 548, 556
Sodium chloride, as standard substance, 568
  for standardizing silver, 569
  inclusion of water by, 164
Sodium hydroxide, as flux, 399
  standardization of, 553
  standard solution of, 550
Sodium nitroprusside indicator, 479
Sodium oxalate,
  for standardizing acids, 549
    permanganate, 592
  reducing properties of, 591
Sodium peroxide, as flux, 400
Sodium thiosulfate, preparation of solution, 621
  reducing properties of, 590
  stability of solution, 590
  standardization of, 623
  standard solution of, 621
  cf. Thiosulfate
Sodium tungstate, for determining water, 300
Sols, 94
  stability of, 95
Solubility, 48, 49
  and common ion effect, 50
  and complex formation, 58
  and electrolytes, 53
  and hydrogen ion concentration, 61
  and particle size, 102
  and solvent, 57
  and temperature, 56
Solubility product, 48
  of metal sulfides, 64
  table of, salts, 54
  table of, sulfides, 64
Solution of sample, 245
Solvents, in separations, 87
Sorption, 134
Specific gravity, of acids and ammonia, 764, 765
Spectrography, 691
Spectrophotometer, 662
Spectrophotometer, photoelectric, 665
Spectrophotometry, 662
  theory of, 646
Spectroscope, 691
Spectroscopy, 691
Standardization, 440
Standard samples, 289
Standard solutions, 431
  preparation of, 440
Standard substances, 441
Standard temperature for volumetric glassware, 525
Stannous tin, determination of, iodimetric, 635
  reduction with, 600
Starch solution, as indicator, 618
Statement of analysis, 16
  in silicate rock analysis, 760
Steam bath, 183
Steel, analysis of, 705
Stirring rods, 193
Stoichiometry, 15
Strontium, separation from calcium, 348, 745
Strontium carbonate, solubility product of, 54
Strontium oxalate, solubility product of, 54
Strontium sulfate, solubility product of, 54
Sublimation, separations by, 87
  purification of solids by, 168
Substitution method of weighing, 216
Succinate method, precipitation by, 71
Sulfides,
  determination of, argentimetric, 574
    iodimetric, 634
    with hypochlorite, 588
  determination of sulfur in, 342
  postprecipitation of, 113
  precipitation of, 63
  solubility products of, 64
  cf. Hydrogen sulfide
Sulfite, determination of, iodimetric, 634
Sulfur, contamination by, 342
  determination of, chronometric, 685
    gravimetric, as barium sulfate, 329
      in alkali salts, 340

- Sulfur — *Continued*
  - determination of, gravimetric — *Continued*
    - in presence of iron, 337
    - in pyrite, 343
    - in rocks, 759
    - in soluble sulfates, 340
    - in steel, 718
  - turbidimetric, 690
  - volumetric, 574, 588, 634
    - in steel, 719
  - oxidation of, in grinding sample, 343
  - cf. Sulfate, Sulfide, Sulfite
- Sulfur dioxide, as reducing agent, 597, 739
  - cf. Sulfite
- Sulfuric acid,
  - density of, 764, 765
  - ionization constant of, 37
  - use as desiccant, 190
  - volatilization of, 248
  - cf. Sulfate
- Sulfurous acid, reductions with, 597, 739
  - cf. Sulfite
- Summation of results, 285
  - in rock analysis, 760
- Supersaturation, 99
- Surface condensation, of water, 133
- Surface tension, 686
  - and titrations, 502
- Suspensions, in colorimetry, 651
  - in nephelometry, 689
- Suspensoids, 94
- Swings, method of, in weighing, 207

T

- Tannin, 85
- Tantalum, separation from columbium, 85
- Tares, 222
- Tartaric acid, ionization constants of, 37
- Technique, of common analytical operations, 235
- Temperature, corrections, in volumetric work, 541
  - differences in weighing, 223
  - standard, in calibration of glassware, 524
- Testing, of volumetric ware, 525
  - of weights, 224
- Tetraphenylarsonium chloride, 85
- Thallium, cf. Thallous
- Thallous bromide, solubility pro of, 54
- Thallous chloride, solubility pro of, 54
- Thallous iodate, solubility produ 54
- Thallous iodide, solubility produ 54
- Thallous sulfide, solubility produc 64
- Thallous thallium, reaction bromate, 637
- Theorem of Le Chatelier-van't H 33
- Thermometric methods, 685
- Thiocyanate,
  - determination of, argentimetric,
    - gravimetric, 313
    - mercurimetric, 480
- Thioglycolic β-amino naphthalide,
- Thionalide, 85
- Thiosulfate,
  - reaction with hypochlorite, 588
  - reaction with iodine, 619
  - cf. Sodium thiosulfate
- Thymol blue, 448
- Thymolphthalein, 448
- Tin, determination of, in brass, 69
  - cf. Stannous tin
- Tirrill burner, 182
- Titanium,
  - determination of, colorimetric, silicate rocks, 742
    - gravimetric, 744
  - reduction of, 498
  - separation of, from various ments, 76
- Titanium solution, standard, 742
- Titanous chloride, 588
- Titration, 431, 538
  - in absence of carbon dioxide, 53
  - error, 432
- Titrations, amperometric, 513
  - colorimetric, 654
  - conductometric, 509
  - of standard acid with stand base, 555
  - performance of, 538
  - physico-chemical, 501
  - potentiometric, 502
- Tolerances, of weights, 206
  - of volumetric glassware, 522
- Tongs, crucible, 194
- Transmission coefficient, 646

ansposition, method of weighing, 215
Triangles, 194
  glass, 248
Trip scale, 201
Tropeoline 00, 448
Tungsten, determination of, in steel, 728
Tungstic oxide, correction for impurities in, 729
  ignition of, 729
Turbidimeter, 688
Turbidimetry, 688
Turbidity, and end point, 469
Tyndall effect, 93

U

Ultrafilters, 94
U. S. Bureau of Standards samples, 289
Units, of capacity, 524
  of mass, 205
Uranium, determination of, volumetric, 609
  oxidation potential of, 483
Uranyl zinc acetate solution, reagent for sodium, 416
Urea, determination of, with hypochlorite, 588
  for adjusting acidity, 108, 347
  reaction of, with nitrous acid, 629

V

Vacuo, reduction of weights to, 218
Vanadate, oxidation potential of, 483
  titration with iron, 609
Vanadium,
  determination of,
    in steel, 724
  interference of, in iron titration, 601, 748
    in phosphorus determination, 394, 755
  reduction of, 498
Vapor pressure, of water, 127
  salt hydrates, 128, 132
Viscosimetric titrations, 502
Viscosity, 686
Volatilization, separation by, 86
  methods, 24
Volhard titration, application of, 573
  theory of, 475
Volt, 144
Voltmeter, 144
Volume, of precipitate, determination of, 678
Volumetric analysis, general discussion of, 431
  limitations of, 433
  methods, 432
Volumetric glassware, calibration of 524
  specifications for, 522
  tolerances for, 522
  use of, 535
Vycor, 174

W

Walpole comparator, 661
Wash bottle, 191
Washing of precipitates, 252
Watch glasses, 193
Water, adsorbed, 132
  density of, 764
  determination of,
    gravimetric, direct, 301, 304
      indirect, 299
    hygroscopic, 299
    in barium chloride dihydrate 300
      rocks, 752
      sodium bicarbonate, 303
    volumetric, 305
  dissociation of, 37
  distilled, 170
  essential, 138
  hygroscopic, 118, 134, 136
    determination of, 299
      in silicate rocks, 752
  inclusion of, 164
  in equilibrium with air, 552
  in liquids, 305
  in solids, 136
  ionization product of, 38
  loss on grinding, 240
  non-essential, 136
  occluded, 136
  of constitution, 138
  of crystallization, 138
  of imbibition, 134, 137
  state of, in solids, 136
  vapor pressure of, 127
Weighing, accuracy of, 205, 216, 245
  bottle, 242
  errors in, 216
  forms, 27

Weighing — *Continued*
  methods of,
    microchemical, 214
    ordinary, 211
    short swings, 212
    single deflection, 213
    substitution, 216
    swings, 207
    transposition, 215
  reduction of, to vacuo, 218
  scoop, 244
Weighing the sample, 241
Weight buret, 542
Weights, 205
  calibration of, 224
  care of, 233
  tolerances of, 206
Witt plate, 186

X

X-ray spectrography, 693

Z

Zero point, of balance, 207, 21
Zimmermann-Reinhardt soluti
Zinc,
  determination of, argenti 574
    gravimetric, as pyrophos 373, 703
    in brass, 703
    mercurimetric, 576
    volumetric, as ferrocyanid
  separation of, from copper, 70
Zinc ammonium phosphate, solu of, 373
Zinc oxide, suspension, 71
Zinc sulfide, postprecipitation o
Zirconium,
  determination of, as oxide, 32
    as phosphate, in rocks, 758
  separation of, 76, 82, 83, 757
Zirconium phosphate, precipit of, 758, 759

C NL 241412 [illegible] 25.8.59

KB
16-4-97

C.F.T.R.I. LIBRARY, MYSORE–13

Acc.No. 1281

Call No. E1,1:3;R N50

Please return this publication on or before the last
DATE stamped below to avoid incurring overdue cha

Due date	Return Date	Due Date	Return Da
29/8	19.8.92	28 SEP	1997 3
5.9.92	7.9.92	19/10/97	8/10/
7.10.92	7/10	13/11/98	2/11/
5.3.93	16.3.93	23/9/99	23
19.6.93	7.6.93	7/10/99	7/10
PP. 144		22.10.99	[illegible]
30.7.94	2/8/94	3/11/99	
11.4.95	29.3.95	12/5	2n 12/
3/7/97	1/7/97	26/5	2n 25
1.98	7/4/98		

24.2.2003, 24.2.03 21.4.2003, 21.4

10.3.2003 10.3.03 5.5.2003, 8-5-

21.3.03 [illegible] 22.5.2003 22

Acc. No. 1281
E4, 1=31R
OLTHOFF
lance of
[illegible]